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OXYGEN ISOTOPE RATIOS OF CONTEMPORARY WATERS AND DIATOM SILICA: *IMPLICATIONS FOR PALAEOCLIMATE RESEARCH*

Thesis submitted for the degree of Doctor of Philosophy in the University of London *by*

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Abstract

Despite the increasingly frequent use of oxygen isotopes in diatom silica as a proxy for past environmental change, the processes which control these isotope ratios remain poorly understood. Various factors affect the oxygen isotope composition of sedimentary diatom silica, beginning with the atmospheric changes that determine the isotope composition of precipitation through the controls over assimilation of silica within the diatom cell to the processes affecting silica sedimentation and diagenesis. An understanding of these contemporary processes is an important prerequisite for the use of lake sediment records as archives of past climate change. The aim of this thesis was to investigate the cascade of factors which determine the oxygen isotope composition of sedimentary diatom silica, using a case study of Lochnagar, a remote upland lake in Scotland.

The climate-lake interface at Lochnagar was studied using bi-weekly monitoring of the oxygen isotope composition of precipitation ($\delta^{18}O_P$) and lake water ($\delta^{18}O_L$) (between December 1999 and September 2005) and monthly monitoring of the cell density and oxygen isotope composition of living diatoms ($\delta^{18}O_{silica}$) (between May 2004 and November 2005, excluding periods of lake ice cover). Three supplementary datasets of monthly $\delta^{18}O_P$ from sites in Great Britain and Eire (Wallingford, Oxfordshire; Keyworth, Nottinghamshire and Valentia, Kerry) were also analysed to obtain a wider geographic perspective. $\delta^{18}O_{silica}$ was analysed from the surface sediments of a series of lakes across Europe in order to assess the relationship between climate and $\delta^{18}O_{silica}$ over a large continental gradient.

The research demonstrates considerable complexity in the climate-lake-sediment interface at Lochnagar. $\delta^{18}O_P$ is a sensitive climate tracer, reflecting changes in air temperature and precipitation amount, however the response varies with site location. Changes in $\delta^{18}O_L$ at Lochnagar reflected changes in $\delta^{18}O_P$, but the response was mediated by limnological processes, primarily the water throughflow rate, which is a function of precipitation amount. Diatom abundance varied markedly over the annual cycle, with peak abundance during Spring, leading to a probable seasonal bias in the sediment $\delta^{18}O_{silica}$ record. $\delta^{18}O_{silica}$ values also fluctuated markedly throughout the seasonal cycle, although no systematic relationship with potential physical controls was observed. However, $\delta^{18}O_{silica}$ values in the surface sediment dataset do correlate with the continental climate gradient, suggesting that diagenetic effects play an important role in fixing the climate signal.

The thesis concludes that potential does exist for the use of $\delta^{18}O_{silica}$ in palaeoclimate research, despite considerable complexity within the sediment-climate interface. The processes which combine to determine the sedimentary $\delta^{18}O_{silica}$ signal are combined in a basic holistic model to enable a more rigorous approach to interpreting the $\delta^{18}O_{silica}$ record from Lochnagar. However, further detailed research into controls over isotope fractionation during silica assimilation by diatoms, and subsequent diagenesis, is required if $\delta^{18}O_{silica}$ records are to be confidently used to reconstruct past climate.

Acknowledgements

This work would have been impossible without the significant contribution of many others. Thanks especially to Jo Porter for his tireless endeavours in the field and the tonnes of water he's carried back. Thanks to Viv Jones, Melanie Leng and Rick Battarbee for their advice, encouragement and direction. Thanks to Hilary Sloane, Carol Arrowsmith, Ian Patmore, Tula Maxted and Janet Hope for their help with lab work and analyses. The contribution of Neil Rose, Don Monteith and Ewan Shilland was invaluable, in terms of both data and advice. The advice of Tim Atkinson, Roger Flower, Brenda Thake, Phil Barker, Mike Hughes, Patrick Rioual, Nigel Cameron, John Boyle, Jonathan Holmes, Anson Mackay and Michelle Crenshaw was also much appreciated. Thanks to Gavin Simpson, John Birks, Richard Telford, Einar Heegaard, Richard Chandler and Matt Jones for helping me come to terms, to some extent, with numbers. Thanks to George Swann for his frequent, sometimes productive, discussions and to Dave Morley and Jo Thorpe for their baptism to the world of diatom isotopes. Thanks to Simon Turner, James Shilland, Handong Yang and Oliver Nixon for help with fieldwork. Dirk Sachse, Muriel Bonjean, Shiela Gibbs, Rachel Helliwell, Luis Araguas-Araguas, George Darling, FRS Pitlochry and the BADC are thanked for provision of data and samples. I'm grateful for the money provided by NERC, NIGL, the Marie Curie fund, ENSIS and the UCL Graduate School. Thanks to Carl, Adam, Tom, Patrick, Andy, Gina, Dan, Matt, Gen, Alex, Luo, Hong, Dave E. and everyone at the ECRC, UCL Geography and FBI Bergen for their contributions to morale over the years. Thanks to my family and special thanks to Martha for her constant love and support throughout.

I believe there is someone out there watching us. Unfortunately, it's the government (Woody Allen).

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Chapter 1:

Introduction

1.1 Climate change: past perspectives for understanding the future

Understanding past climate change can play a vital role in addressing the issues concerning future global warming (Houghton *et al.*, 2001; Allen and Ingram, 2002; Arnell *et al.*, 2005; Houghton, 2005). Only through synthesis of long term climate change records can the context of 20th century warming be fully appreciated (e.g. Mann *et al.*, 1998a; 1998b; Mann and Jones, 2003; Moberg *et al.*, 2005). In addition, records of past climate change are necessary for testing and developing the climate models which are used for prediction of future climate change (Goody *et al.*, 1998; Valdes, 2003; Charman *et al.*, 2006; Anderson *et al.*, 2006). Instrumental records provide detail and accuracy in some regions (Manley, 1953; 1974; Parker *et al.*, 1992; Folland *et al.*, 2001), however the limited spatial and temporal coverage of these data requires the use of natural archives (proxy records). Rigorous interpretation of palaeoclimate records from proxy data is therefore of major importance to understanding past and present climate systems, and consequently in predicting future change.

Of all the palaeoclimate proxy records, arguably the most important global findings have been derived from stratigraphic analyses of deep-sea marine

sediments and polar ice (for review see Imbrie and Imbrie, 1979; Lowe and Walker, 1997; Mackay *et al.*, 2003; Oldfield, 2005; Elias, 2007). The deep, continuous deposits of marine sediment document the long term history of the Earth's ocean and climate, most notably the cyclical growth and recession of the polar ice sheets and their link with orbital forcing (Shackleton, 1967; Hays *et al.*, 1976; Imbrie and Imbrie, 1979; Shackleton, 1987). Ice core records from Greenland and Antarctica document high resolution changes in the global water cycle and atmospheric chemistry revealing marked shifts in the climate system over long and short time scales (Dansgaard *et al.*, 1993; Blunier *et al.*, 1995; Petit *et al.*, 1999; Johnsen *et al.*, 2001; Stauffer *et al.*, 2004). However, in order to assess the true global nature of such proxy records, equally robust data from continental archives are required. In particular, marine and polar ice core records can not provide information regarding climate changes on the regional scale and in regions inhabited by humankind.

Continental records of past climate change can be derived from a variety of archives which vary according to their response to specific climate forcing, their temporal and spatial resolution and their suitability to provide accurate chronological control. Examples of continental archives include: geomorphological evidence for past fluvial and glacial activity, tree rings, stratigraphic peat deposits, cave speleothems, ground waters and lake sediments (Lowe and Walker, 1997; Williams *et al.*, 1998; Mackay *et al.*, 2003;

Elias, 2007). The aim of this thesis is to investigate potential climate signals preserved in lake sediments.

1.2 Lakes as archives of past climate

Lake sediments offer considerable value as terrestrial palaeoclimate archives. They are often continuous, undisturbed sediment sequences which span timescales of annual to millennial duration (Tzedakis *et al.*, 1997; Rioual *et al.*, 2001; Bradbury *et al.*, 2002; Ojala and Alenius, 2005; Khursevich *et al.*, 2005). Lakes can be found across all latitudes and altitudes and preserve an abundance of information in their biological, lithological and geochemical remains (Battarbee, 2000; Last and Smol, 2001; Smol *et al.*, 2001a; 2001b - and chapters therein). A major limitation, however, is their extreme sensitivity to human disruption. In Europe, anthropogenic activities influence almost all low-lying freshwater environments. Effects such as deforestation, soil erosion, acidification, leaching of nutrients, salinisation, hydrological modification and toxic pollution mean that there are very few undisturbed lakes, and consequently the record of natural environmental change preserved in the sediments can be complicated by an anthropogenic signal. Remote arctic and alpine lakes, however, experience fewer direct anthropogenic effects, other than long range pollution in some cases, and are therefore considered more sensitive archives of climate variability (Psenner and Schmidt, 1992; Battarbee *et al.*, 2001; Koinig *et al.*, 2002; Smol *et al.*, 2005; Guilizzoni *et al.*, 2006; Schmidt *et al.*, 2006).

Palaeoclimate information can be gleaned from a vast array of lake sedimentary data (Last and Smol, 2001; Smol *et al.*, 2001a; 2001b - and chapters therein). The use of biological remains, for example pollen, diatoms and chironomid head capsules, is most common, offering both qualitative and quantitative records of past climate (Battarbee, 2000). Biological responses to climate change, however, are often non-linear, multifactorial and indirect, therefore interpretation of fossil records in terms of past climate can be ambiguous and subjective. In addition, the use of palaeolimnology to answer questions concerning ecological and environmental response to climate variability over long timescales (e.g. Anderson *et al.*, 1996; Quinlan *et al.*, 2005; Smol *et al.*, 2005; Karst-Riddoch *et al.*, 2005) require climate changes to be determined independent of the biological record. Stable isotope records, in particular the isotopes of oxygen and hydrogen, potentially record climatic changes independent of biological processes (Leng and Marshall, 2004). Stable isotope geochemistry has been used in palaeoclimate research since the work of McCrea (1950) and Urey (Urey *et al.*, 1951) and has subsequently become commonplace - applied to a wide array of sedimentary archives (Leng and Marshall, 2004; Hoefs, 2004; Leng, 2006). Oxygen isotope ratios of water and minerals (i.e. the ratio of ^{18}O to ^{16}O in a given compound) are governed predominantly by thermodynamic properties, which, although complex, can be quantified precisely and with confidence that contemporary relationships persisted in the past (Urey, 1947; O'Neil *et al.*, 1969).

Oxygen isotope ratios are expressed per mille (‰), relative to a standard, using the δ notation, whereby:

$$\delta^{18}O = 1000\left(\frac{R_{sample} - R_{std}}{R_{std}}\right) \quad (1)$$

where R_{sample} and R_{std} are the respective $^{18}O/^{16}O$ ratios of the sample and standard materials. Where waters and biogenic silica are concerned, δ values are expressed relative to standard mean ocean water (SMOW or V-SMOW: Vienna standard mean ocean water), however δ values in calcium carbonates are expressed relative to Pee Dee Belemnite (PDB) (Criss, 1999; Hoefs, 2004).

The most frequent analyses of oxygen isotope ratios in palaeolimnology are made from calcium carbonates such as mollusc and ostracod shells or authigenic calcite minerals (Stuiver, 1970; Siegenthaler and Eicher, 1986; Ito, 2001). However, in addition isotope records can be derived from biogenic silica (usually diatom remains), cellulose (derived from aquatic and terrestrial plants), chitin (from Coleoptera and chironomid remains) and specific organic compounds (Wolfe *et al.*, 2001; Huang *et al.*, 2004; Wooller *et al.*, 2004; Sachse *et al.*, 2004; Leng and Barker, 2006). High altitude and arctic lakes, which are often oligotrophic and acidic, rarely permit the preservation of calcium carbonates, whereas aquatic cellulose is less abundant due to fewer aquatic plants. In such cases, analysis of diatom silica provides an opportunity to derive oxygen isotope

records where alternatives are scarce. Diatoms often play an important role in the primary productivity of such systems (e.g. Flower *et al.* 2007) and a growing volume of research has demonstrated the potential for using oxygen isotopes from biogenic silica as a palaeoclimate tracer from remote alpine and arctic lakes (Shemesh *et al.*, 2001; Barker *et al.*, 2001; Rioual *et al.*, 2001; Hu and Shemesh, 2003; Rosqvist *et al.*, 2004; Jones *et al.*, 2004).

1.3 Oxygen isotope ratios of diatom silica: a reliable palaeoclimate proxy?

The use of stable isotope ratios of biogenic silica as a proxy for past climate and environmental change has expanded greatly over the past decade, aided by developments in sample preparation and analytical techniques (De La Rocha *et al.*, 1997; 1998; Leng *et al.*, 2001; Barker *et al.*, 2001; Morley *et al.*, 2004; Haug *et al.*, 2005; Lucke *et al.*, 2005; Tyler *et al.*, 2006; Lamb *et al.*, 2006; De La Rocha, 2006). In theory, the ratio of $^{18}O/^{16}O$ in diatom silica reflects the temperature and oxygen isotope composition of formation waters (lake or ocean water) and consequently offers a record of past hydrologic, oceanic and climate change (Leng and Barker, 2006). However, despite the frequent use of oxygen isotopes in diatom silica as a proxy for past environmental change, the processes which control these isotope ratios remain poorly understood (Leng and Barker, 2006). In particular, consensus has yet to be reached over oxygen isotope fractionation during diatom silica uptake and frustule formation. Isotope

fractionation is the physical phenomenon which, during chemical reactions or changes in state, causes alteration to the relative abundance of certain isotopes (i.e. ^{18}O and ^{16}O) due to their difference in mass (Hoefs 2004). Diatoms form their silicate frustules from silica dissolved in water (e.g. orthosilicic acid, H_4SiO_4). The oxygen isotope composition of dissolved silica is assumed to reflect the oxygen isotope composition of the water, due to the free exchange of oxygen between water and dissolved silica (Brandriss *et al.*, 1998; Felipe *et al.*, 2004). However, diatom silica invariably has an $^{18}O/^{16}O$ ratio greater than that of formation water, indicating the preferential assimilation of the heavier ^{18}O isotope. Furthermore, the degree of difference between the $^{18}O/^{16}O$ ratio of water and diatom silica is believed to vary with temperature, as is the case with many mineral types, including quartz and amorphous silica (Clayton *et al.*, 1972; Labeyrie, 1974; Kawabe, 1978; Kita *et al.*, 1985; Hoefs, 2004). However, to date the fractionation of oxygen isotopes between diatom silica and water is poorly quantified (Leng and Barker, 2006). In addition, factors such as the effect of diatom taxon, growth rate and pH on oxygen isotope fractionation are yet to be fully investigated (Leng and Barker, 2006).

The use of oxygen isotope ratios in biogenic silica ($\delta^{18}O_{silica}$) as a palaeoclimate proxy has been hindered in the past by methodological issues. In particular, procedures for (a) obtaining pure biogenic silica, uncontaminated by organic and mineral fractions and (b) treatment of the outer hydrous layer of diatom frustules - which exchanges oxygen freely with ambient water - have only recently reached

an acceptable level of standardisation (Leng *et al.*, 2001; Lucke *et al.*, 2005; Leng and Barker, 2006).

Small amounts of mineral contaminants within diatom silica samples can lead to marked alterations in $\delta^{18}O_{silica}$ values (Morley *et al.*, 2004), an issue which may have been overlooked by early research. In many cases, such mineral contamination can be removed through a process of sieving, gravitational settling and heavy liquid separation (Morley *et al.*, 2004). Alternatively, gravitational split-flow thin fractionation (SPLITT), which exploits the different hydrodynamic properties of sediment particles by passage through a narrow laminar flow channel, can also be effective in separating diatoms from mineral grains, but only where a good concentrate has first been achieved by standard methods (Rings *et al.*, 2004; Leng and Barker, 2006). Where mineral contamination can not be physically removed, it may be possible to isolate the diatom silica signal from the contaminated $\delta^{18}O_{silica}$ value using chemical mass balance calculations (Lamb *et al.*, 2006).

The silica structure of diatom frustules has led to further complications to the method development for $\delta^{18}O_{silica}$ analyses. Diatom silica frustules consist of an inner tetrahedrally bonded silica skeleton (Si-O-Si) surrounded by an outer hydrous silica layer (Labeyrie and Juillet, 1982; Leng and Barker, 2006; Figure 1.1). The outer hydrous silica readily exchanges oxygen isotopes with any water it comes into contact with and therefore has a marked effect on $\delta^{18}O_{silica}$ values

(Juillet, 1980a; 1980b). The majority of laboratories liberate oxygen from silica by reaction with strong fluorine reagents (fluorination), however a range of approaches have been taken in order to counteract the effects of exchangeable hydrous silica on $\delta^{18}O_{silica}$ measurements. These include: (i) simple vacuum dehydration (Labeyrie, 1974; Brandriss *et al.*, 1998); (ii) controlled isotope exchange (CIE) whereby the sample is exposed to water of a known isotope composition prior to analysis and the effect of the hydrous silica accounted for using mass balance calculations (Labeyrie and Juillet, 1982; Juillet-Leclerc and Labeyrie, 1987; Shemesh *et al.*, 1992) and (iii) stepwise fluorination, where a stepped reaction with a stoichiometric deficiency of fluorine reagent is used to strip the outer hydrous silica layer prior to analysis of the inner silica skeleton (Matheney and Knauth, 1989; Leng *et al.*, 2001; Leng and Barker, 2006). (iv) Inductive high temperature carbon reduction (iHTR), is a new method which removes the hydrous silica by heating at lower temperatures (850-1050°C) before graphite reduction of the structural silica, as an alternative to fluorination (Lucke *et al.*, 2005). To date, the most commonly published method is stepwise fluorination (Leng *et al.*, 2001), where repeated measurements have enabled the development of a routine methodology with accompanying improvements in the accuracy and precision of results over a number of years (M. Leng pers. comm.).

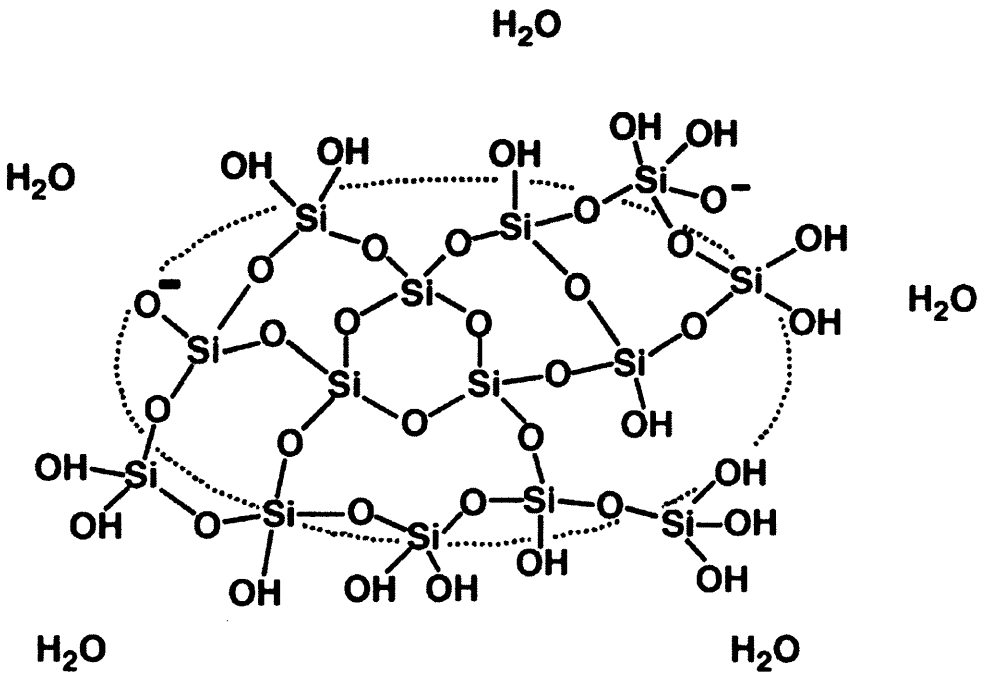

Figure 1.1: A schematic illustration of the structure of amorphous hydrated silica (i.e. diatom silica) showing the inner tetrahedrally bonded silica and the outer (readily exchangeable) hydrous layer. Taken from Leng and Barker (2006), modified from Perry (1989).

As a consequence of the methodological issues outlined above, the results of early attempts at calibrating the fractionation of oxygen isotopes during diatom formation proved largely inconclusive. A broad range of responses have been observed, with suggested temperature coefficients over silica-water isotope fractionation ranging from ~ –0.2‰/°C to ~ –0.5‰/°C (Labeyrie, 1974; Juillet-Leclerc and Labeyrie, 1987; Matheney and Knauth, 1989; Shemesh *et al.*, 1992; Brandriss *et al.*, 1998; Moschen *et al.*, 2005; Figure 1.2). The most recent attempts at calibrating oxygen isotope fractionation in diatom silica have been carried out by Brandriss *et al.* (1998) using culture experiments on a small range of diatom taxa, and Moschen *et al.* (2005) who measured $\delta^{18}O_{silica}$ from monthly diatom samples in Lake Holzmaar, Germany. Both studies suggest a ~ –0.2‰/°C

temperature fractionation coefficient between diatom silica and lake water (Brandriss *et al.*, 1998; Moschen *et al.*, 2005). However, these studies differ in the analytical procedures used to analyse the oxygen isotopes, and neither study used the stepwise fluorination method, most commonly implemented with sediment material (Leng and Barker, 2006). Therefore, further research is required to fully assess the environmental controls over $\delta^{18}O_{silica}$ values.

An additional unknown factor is the effect of diagenesis on $\delta^{18}O_{silica}$ values. By comparing $\delta^{18}O_{silica}$ analysed from marine phytoplankton tows with the $\delta^{18}O_{silica}$ values of surface sediment on the ocean floor, Schmidt *et al.* (1997) observed a marked offset between the two, associated with an increase in $\delta^{18}O_{silica}$ during sedimentation. Schmidt *et al.* (2001) demonstrated that the $\delta^{18}O_{silica}$ offset is correlated with opal maturation – the dehydration of hydroxyl Si-OH silica to form Si-O-Si bonded silica. Moschen *et al.* (2006) observed a similar offset between lake phytoplankton diatom silica and surface sediments. Laboratory experiments demonstrated that dissolution of diatom frustules in alkali solution (pH 9) can lead to modification of $\delta^{18}O_{silica}$ values, however such effects are reduced when diatoms retain their organic cell coating during sedimentation, and effects are thought to be negligible in neutral or acidic conditions (Moschen *et al.*, 2006).

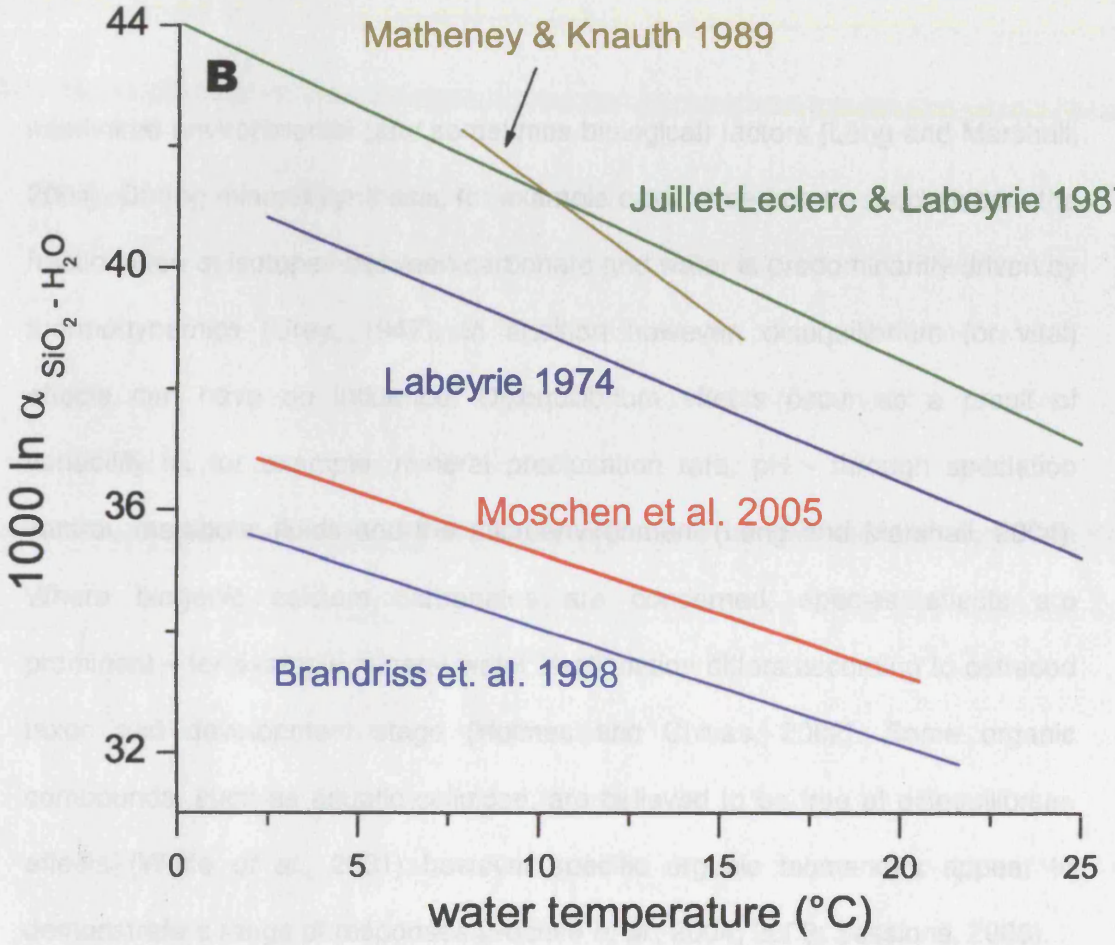

Figure 1.2: Various silica-water fractionation factor vs. temperature calibrations resulting from previous research. Adapted from Moschen *et al.* (2005).

1.4 Interpretation of lake sediment oxygen isotope records

In general, the ratio of oxygen isotopes in lake sediment components record the oxygen isotope composition of lake water plus the effects of isotope fractionation (often temperature dependent) during the formation of the organic or inorganic organic compound analysed. However, both lake water isotope composition and compound-water isotope fractionation are influenced by a wide range of

interlinked environmental (and sometimes biological) factors (Leng and Marshall, 2004). During mineral synthesis, for example calcium carbonate precipitation, the fractionation of isotopes between carbonate and water is predominantly driven by thermodynamics (Urey, 1947). In addition however, disequilibrium (or vital) effects can have an influence. Disequilibrium effects occur as a result of variability in, for example, mineral precipitation rate, pH - through speciation control, metabolic fluids and the microenvironment (Leng and Marshall, 2004). Where biogenic calcium carbonates are concerned, species effects are prominent – for example mineral-water fractionation differs according to ostracod taxon and development stage (Holmes and Chivas, 2002). Some organic compounds, such as aquatic cellulose, are believed to be free of disequilibrium effects (Wolfe *et al.*, 2001) however specific organic biomarkers appear to demonstrate a range of responses (Sachse *et al.*, 2004; 2006; Sessions, 2006).

Lake waters themselves represent the isotope composition of precipitation, modified as a function of climate and residence time within the lake and catchment. Some lake waters are predominantly fed by groundwater, which, unless subject to mixing with subsurface waters in tectonically active regions, represent a weighted averaged signal of precipitation. The most effective mechanism by which lake waters are modified with respect to precipitation is via evaporative enrichment of surface waters (Gat, 1995). In such situations, isotope ratios of lake waters (and consequently sedimentary isotope ratios) reflect the

balance between precipitation and evaporation, and can consequently be used as a tool to reconstruct past lake water balance (Talbot, 1990; Lister *et al.*, 1991). In many open-system temperate lakes however, evaporation plays a lesser role in effective water balance and lake water isotope ratios are more closely related to isotopes in precipitation. In such circumstances, lake sediment records potentially track past isotopes in precipitation – a proxy which is sensitive to climate, is well constrained theoretically, is replicable at the regional scale and can link directly with atmospheric global climate models (AGCMs) (e.g. Joussaume *et al.*, 1984; Jouzel *et al.*, 1991; 2000). In temperate and high-latitude regions, oxygen isotopes in precipitation ($\delta^{18}O_P$) records are usually interpreted as reflecting changes in surface air temperature (Dansgaard, 1964; Rozanski *et al.*, 1993; von Grafenstein *et al.*, 1996; Wooller *et al.*, 2004). However, the climatic controls over $\delta^{18}O_P$ are complex and varied and can reflect changes in moisture source (Edwards *et al.*, 1996; Hammarlund *et al.*, 2002; Jones *et al.*, 2004) and precipitation amount (Barker *et al.*, 2001; Leng and Marshall, 2004).

1.5 Aims and objectives of this research

Oxygen isotope ratios of diatom silica preserved in the sediments of remote mountain lakes offer great potential for tracing past climate changes in temperate regions such as Europe. However, in order to make reliable interpretation from lake sediment records, a solid understanding of the modern processes which operate to construct the sediment record is vital. Between water falling as

precipitation, and biogenic silica deposits forming in the sediment, a cascade of processes operate to determine the eventual signal (Figure 1.3). The major steps in the transmission of climate signals through the system are: 1) The relationship between $\delta^{18}O_P$ and climate variability; 2) The relationship between $\delta^{18}O_L$ and $\delta^{18}O_P$ and the environmental factors which affect this relationship; 3) The effect of seasonal changes in diatom abundance in creating bias in sediment $\delta^{18}O_{silica}$ records; 4) The fractionation of oxygen isotopes between lake water and diatom silica and the effect of water temperature and other chemical and biological variables on the silica-water isotope fractionation. It is the objective of this PhD to investigate these processes through monitoring of a contemporary lake system, and to highlight important considerations which may influence wider research in the field. The research will primarily focus on Lochnagar, an upland loch in eastern Scotland which has been the subject of intensive limnological and palaeolimnological research over the past two decades (discussed in Chapter 2).

The specific aims of this research are:

A) Investigate the climate controls over monthly and annual $\delta^{18}O_P$ for precipitation at Lochnagar and three other stations in the British Isles (Keyworth, Valentia and Wallingford) for which longer monitoring records are available. Discussed in Chapter 4, a multivariate approach was taken, where local climate and regional air flow circulation indices and monthly $\delta^{18}O_P$ datasets were used to develop empirical models for $\delta^{18}O_P$ at each site.

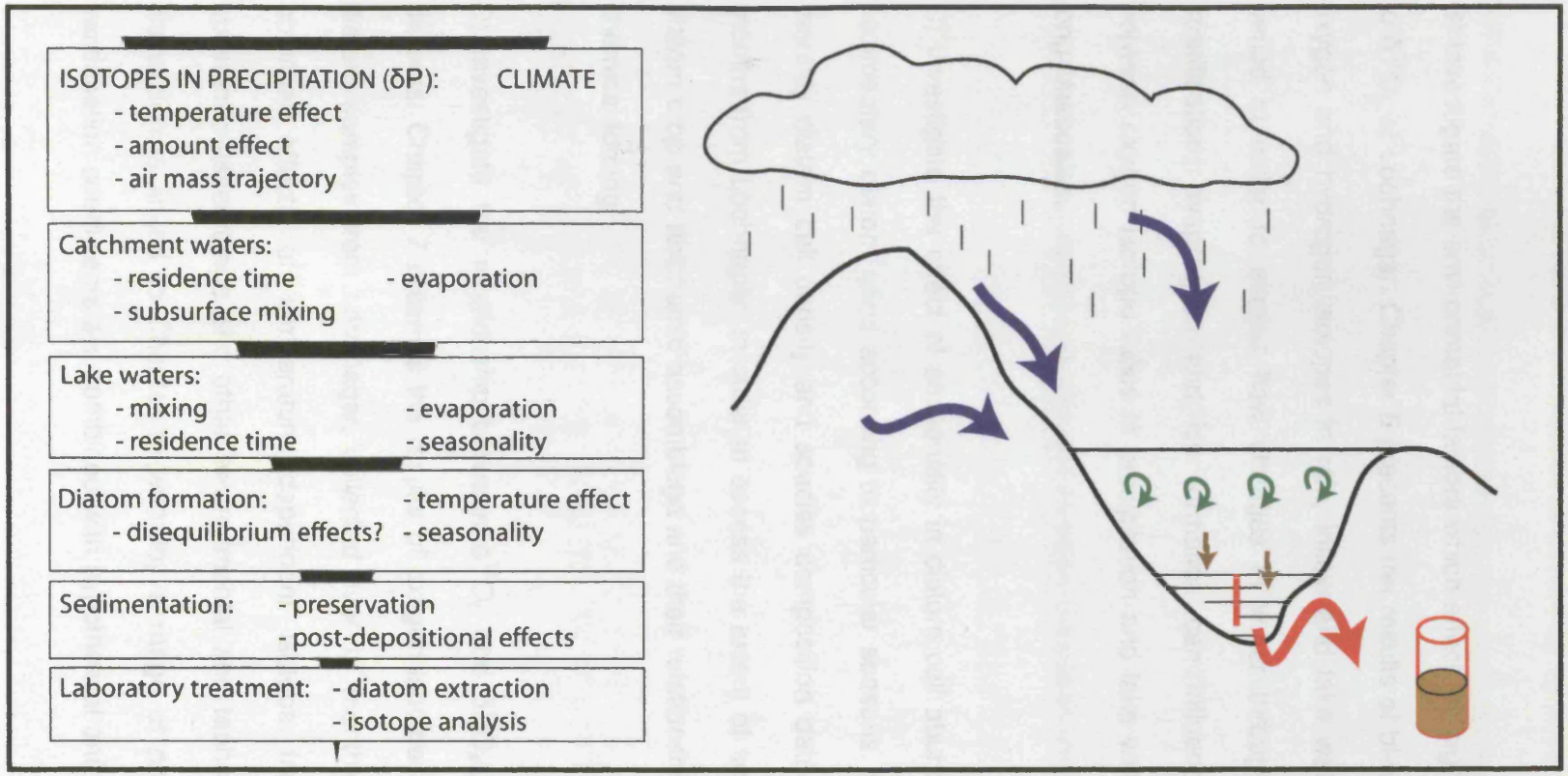

Figure 1.3: Schematic diagram illustrating the cascade of climate signals through the lake system leading to formation of a biogenic silica oxygen isotope record.

B) Investigate the environmental factors which affect the signal transfer of $\delta^{18}O_P$ to $\delta^{18}O_L$ at Lochnagar. Chapter 5 presents the results of bi-weekly monitoring of oxygen and hydrogen isotopes in rain, inflow and lake water over a 5.5 year period in order to assess how changes in water throughflow rate, thermal stratification, evaporation and ice formation can influence the relationship between oxygen isotope ratios in precipitation and lake waters over short and long timescales.

C) Investigate the effect of seasonality in diatom cell abundance on weighting sedimentary diatom silica according to particular seasons. Chapter 6 presents monthly diatom cell density and species composition data, collected over 17 months from Lochnagar, in order to assess the extent of seasonal variability in diatom crop and taxonomic assemblage and their relationship with physical and chemical forcing.

D) Investigate the relationship between $\delta^{18}O_L$ and $\delta^{18}O_{silica}$ of contemporary diatoms. Chapter 7 presents the results of oxygen isotope analysis of monthly diatom samples from Lochnagar, collected over 17 months, and explores the potential effects of temperature dependent isotope fractionation, diatom taxonomic assemblage and other environmental and taphonomic agents. The discussion is linked to Chapter 6, whereby a range of potential temperature fractionation coefficients are combined with hypothetical and observed seasonal

diatom growth to investigate the effect of seasonality on sediment $\delta^{18}O_{silica}$ values.

E) To investigate the relationship between $\delta^{18}O_L$ and sediment $\delta^{18}O_{silica}$ values and the extent to which relationships observed in contemporary systems apply to the sedimentary signal. Chapter 8 presents $\delta^{18}O_{silica}$ data obtained from analysis of lake surface sediments across a wide European climatic gradient and discusses how the broad climate variability is expressed in the sedimentary $\delta^{18}O_{silica}$ values.

F) A further aim of this study is to continue method development for the use of $\delta^{18}O_{silica}$ in palaeoclimate research. In this regard, two experiments were designed to a) test the effect on $\delta^{18}O_{silica}$ of laboratory treatments for the removal of organic matter from sediment samples and b) explore the potential for 'spiking' diatom silica samples with quartz silica of known isotope composition, to enable the analysis of samples smaller than the current 5 mg limit. The results of these experiments are presented in Chapter 3 (Section 3.3.1) and the findings subsequently applied in Chapters 7 and 8.

Overall, the findings are synthesised in Chapter 9, where a simple holistic model is proposed to explain the cascade of the climate signal through to the lake sediments at Lochnagar. Using this model, the sedimentary $\delta^{18}O_{silica}$ response to climate forcing over the recent instrumental period (1881 - 2005) is hind-cast for

comparison with the sediment record for the same period. The number of processes interacting within the climate-lake system make simple palaeoclimate interpretations based on the traditional, single-variable approach difficult to justify. As an alternative, it is suggested that continued efforts to develop whole system models such as that proposed in Chapter 9 represents a more rigorous approach to palaeoclimate research.

Chapter 2:

Selection and description of study site

2.1 Site selection

The wider aim of this research was to investigate limnological responses to environmental forcing in a contemporary system in order to improve interpretation of past climate change from lake sediments. Therefore the primary criterion for site selection was a lake free of marked human impacts, so that the palaeo- lake and catchment system could be assumed analogous to that of the present. In addition, it was important that the study site be accessible for regular monitoring visits to be carried out. In western Europe, undisturbed lakes are rare and restricted to high altitude regions (Chapter 1). The majority of such sites in the United Kingdom are found in upland regions, particularly in Scotland. Lochnagar is a remote and relatively pristine loch (lake), lying at an altitude of 788 m asl in the eastern Highlands of Scotland (Latitude 56.959°N; Longitude 3.231°W; National Grid Reference NO 252 859) (Figure 2.1). With no evidence for any land-use change or active land management within the catchment (Yang *et al.*, 2002b), it is a perfect site for the study of lake interactions with climate and atmospheric chemistry (Rose, 2007). Although there is evidence for the impact of long range transport of airborne pollutants (Yang *et al.*, 2001a; 2002b; Vives *et al.*, 2004), the physical characteristics of the loch and catchment are likely to

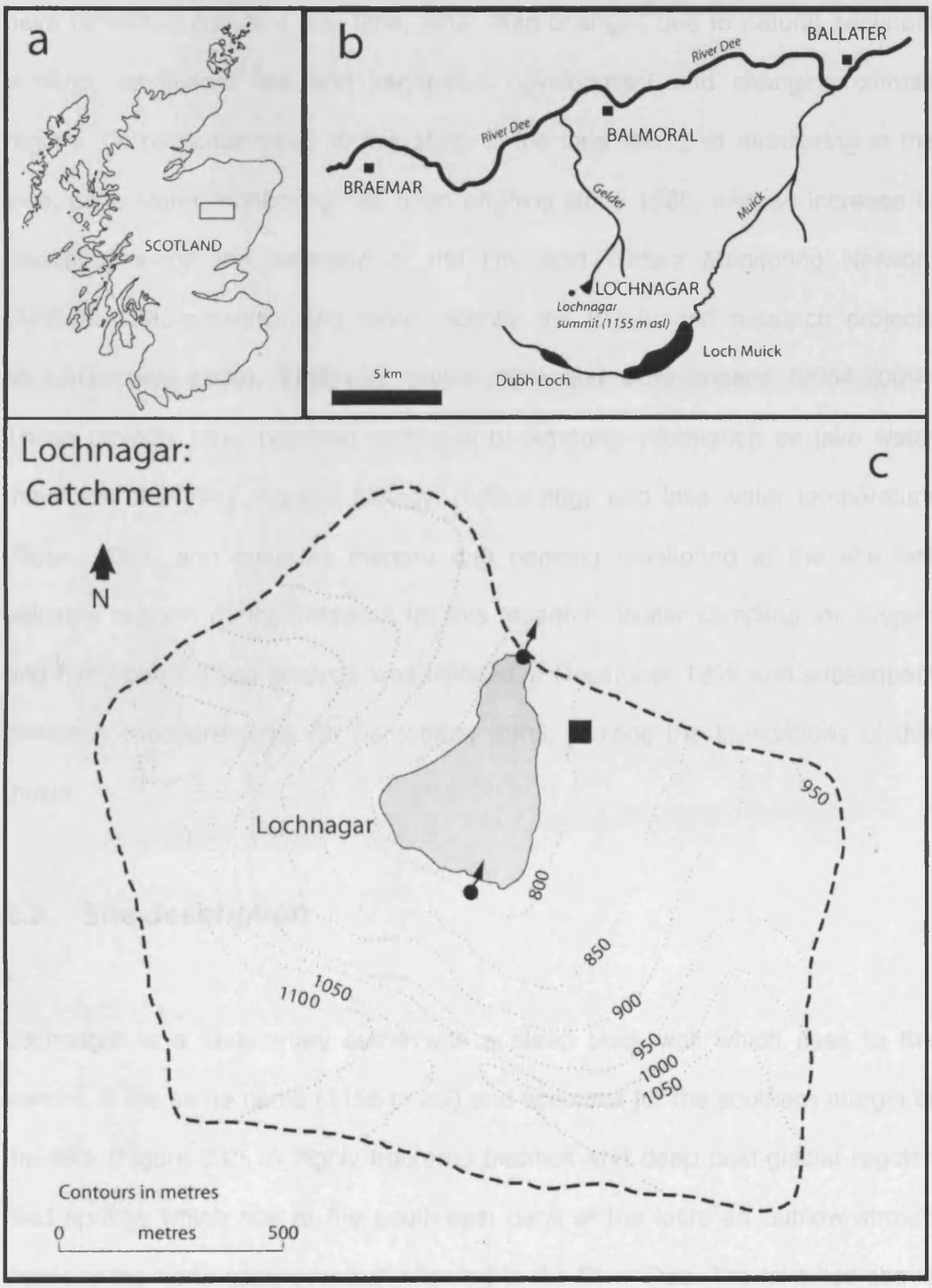

Figure 2.1: Location of Lochnagar (a) within Scotland; (b) with regard to the major hydrological features and towns, and (c) catchment topographical map indicating inflow and outflow stream sampling points (circles) and automatic weather station location (square).

have remained constant with time, other than changes due to natural sediment in-filling, catchment soil and vegetation development and changing climate regime. Of particular value to this study is the long record of monitoring at the loch. Lake water monitoring has been ongoing since 1980, with an increase in frequency since the inception of the UK Acid Waters Monitoring Network (AWMN: 1988-present), and more recently the EU funded research projects MOLAR (1996-1999), EMERGE (2000-2003) and Euro-limpacs (2004-2009). These projects have provided extensive background information on lake water major ion chemistry, aquatic biology, meteorology and lake water temperature (Rose, 2007, and chapters therein) and ongoing monitoring at the site lent valuable support during fieldwork for this research. Water sampling for oxygen and hydrogen isotope analysis was initiated in December 1999 and subsequent bi-weekly measurements (to September 2005) provide the foundations of this thesis.

2.2 Site description

Lochnagar is a Quaternary corrie with a steep back wall which rises to the summit of the same name (1155 m asl) and accounts for the southern margin of the lake (Figure 2.2). A highly fractured bedrock and deep post-glacial regolith feed springs which rise at the south-east bank of the loch, an outflow stream drains to the north-east, eventually flowing to the River Dee. The lake lies above the potential tree line (ca. 650 m asl) and has a sparse catchment vegetation

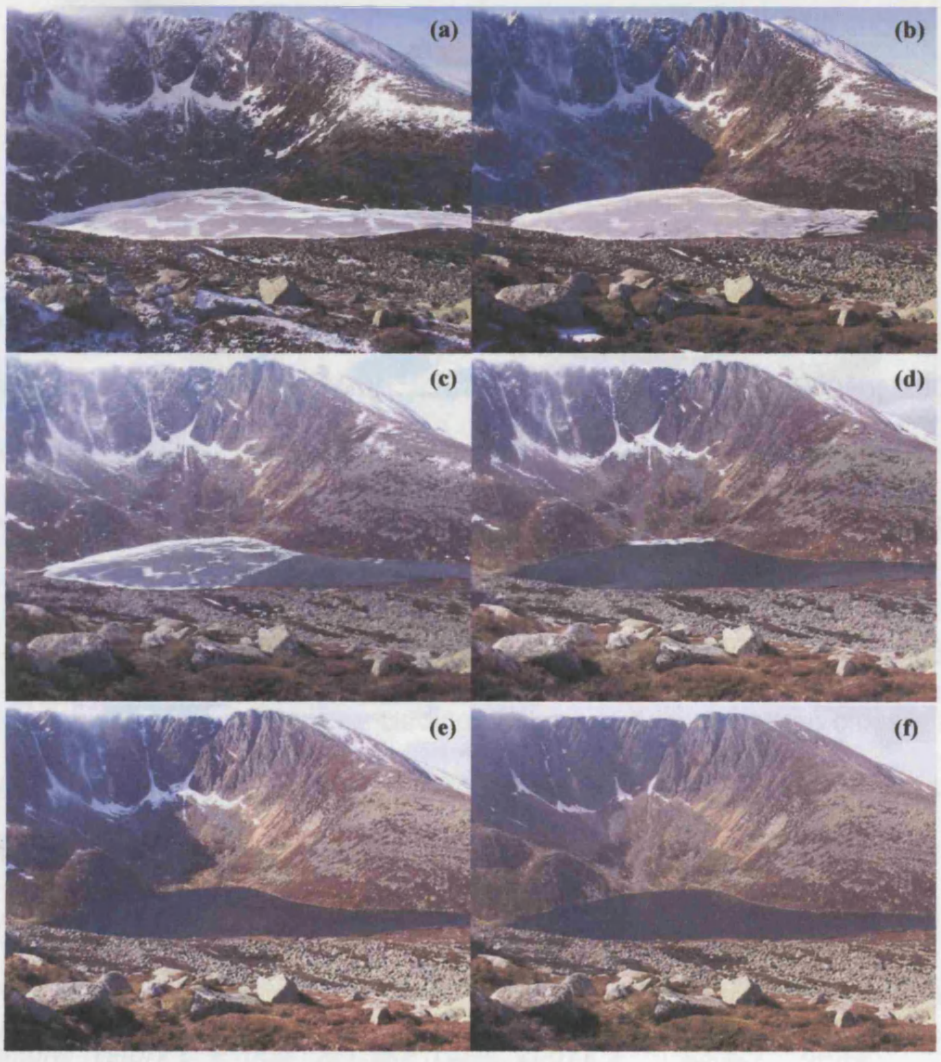

Figure 2.2: Lochnagar taken by automatic camera in 2003 (from Thompson *et al.* 2007). (a) – (f) are 6th, 18th, 22nd, 29th and 30th March and 18th April respectively.

consisting of *Calluna* (heather) *Vaccinium* and a number of mosses and lichens (Birks, 2007). The catchment consists of biotite granite (Goodman, 2007), overlain in places by shallow blanket peat interspersed with extensive boulder fields and scree (Figure 2.2).

2.2.1 Previous work conducted at Lochnagar

The majority of publications related to Lochnagar concern evidence for the deposition of atmospheric pollution (Jones *et al.*, 1993; Helliwell *et al.*, 2001; Jenkins *et al.*, 2001; Rose *et al.*, 2001a; 2001b; Yang *et al.*, 2001b; 2001a; 2002b; 2002a; 2002c; 2003a; 2003b; Vives *et al.*, 2004). In addition, however, there has been interest in aquatic biology (Macek *et al.*, 2006) and Quaternary geomorphology (Brazier *et al.*, 1998; Gordon, 2001; Kirkbride, 2005; Everest and Kubik, 2006). Lochnagar's Holocene sedimentary sequence has been studied for an array of biological remains – including diatoms, pollen, plant macrofossils and organic biomarkers (Dalton *et al.*, 2005). Morley *et al.* (2004) used recent lake sediments from Lochnagar to carry out experiments on cleaning methods for analysis of oxygen isotope ratios in diatom silica (see Chapter 7). Much of the previous research at Lochnagar is summarised in the recent volume, *Lochnagar: the natural history of a mountain lake* (Rose, 2007).

2.2.2 Lake and catchment physical characteristics

The physical characteristics of Lochnagar are described in detail by Hughes (2007). In particular, the catchment is characterised by its steep slopes, especially to the southwest, where slopes exceed 50% (Figure 2.3) (Hughes, 2007). The steep catchment leads to rapid runoff and low infiltration of rain water: Jenkins et al. (2001) estimate that 90% of all precipitation flows directly to the

lake. The lake bathymetry is equally steep, with an average depth of 8.4 m and a maximum depth of 26 m (Figure 2.4). The lake has a surface area of 9.8 ha, giving a catchment to lake ratio of 9.4 (Hughes, 2007).

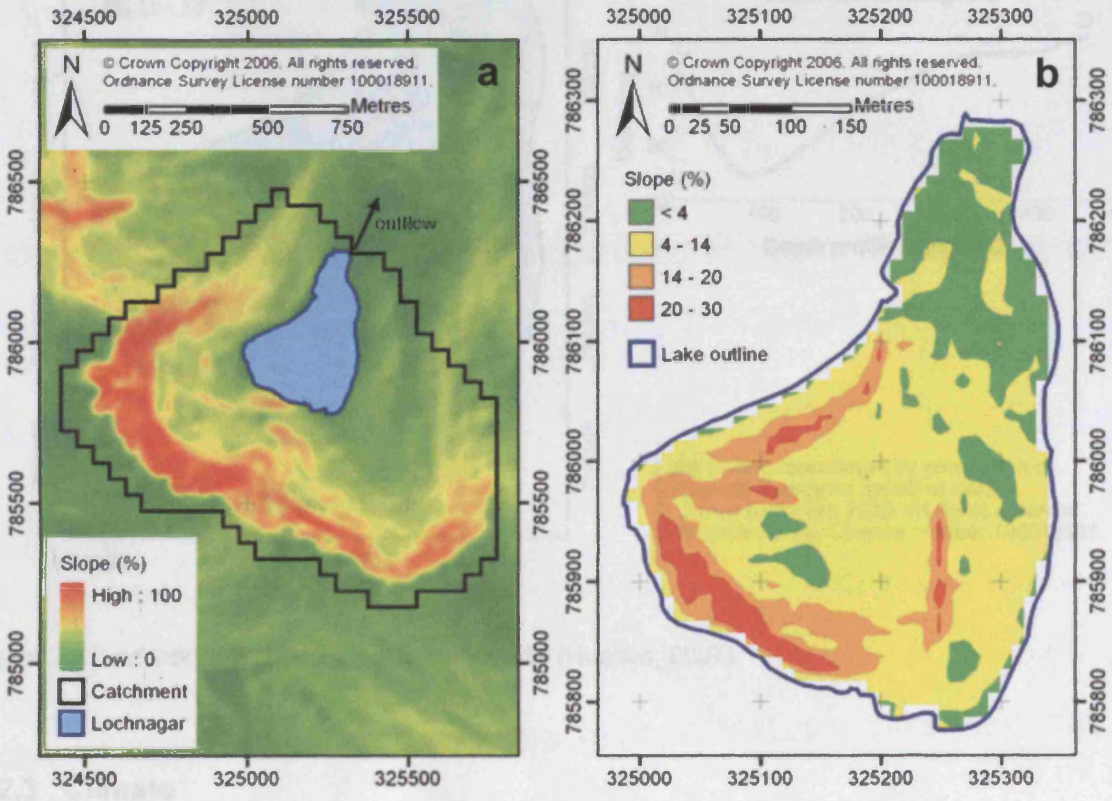

Figure 2.3: Slopes within the Lochnagar catchment (a) and lake (b) (Hughes, 2007).

The steep corrie wall also causes considerable shading, which may have important implications for biological activity within the lake. Hughes (2007) modelled the shading and light environment at Lochnagar for 2005 (Figure 2.5). Certain parts of the catchment, on the south-western wall, are perpetually shaded and hence receive no direct radiation at any point during the year (Hughes, 2007).

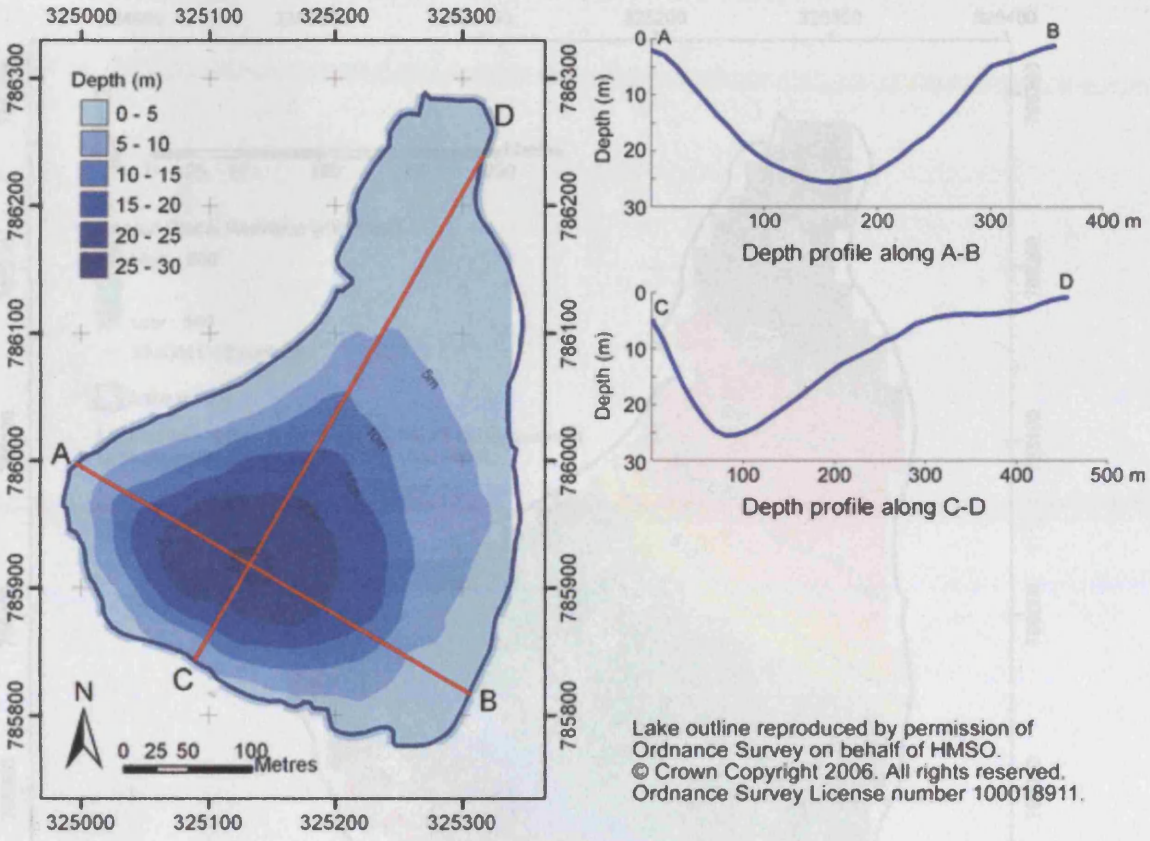

Figure 2.4: Lochnagar bathymetric map and profile (Hughes, 2007).

2.2.3 Climate

The climate of Lochnagar is described by Thompson *et al.* (2007) as having all the characteristic elements of mountain climates; including orographic enhancement of precipitation, valley winds, cold temperatures, and a close association with the free atmosphere (Thompson *et al.*, 2007). Figure 2.6 summarises the seasonal temperature and precipitation amount over the period 1857-2004 at the nearby Braemar station, 12 km to the northwest of Lochnagar

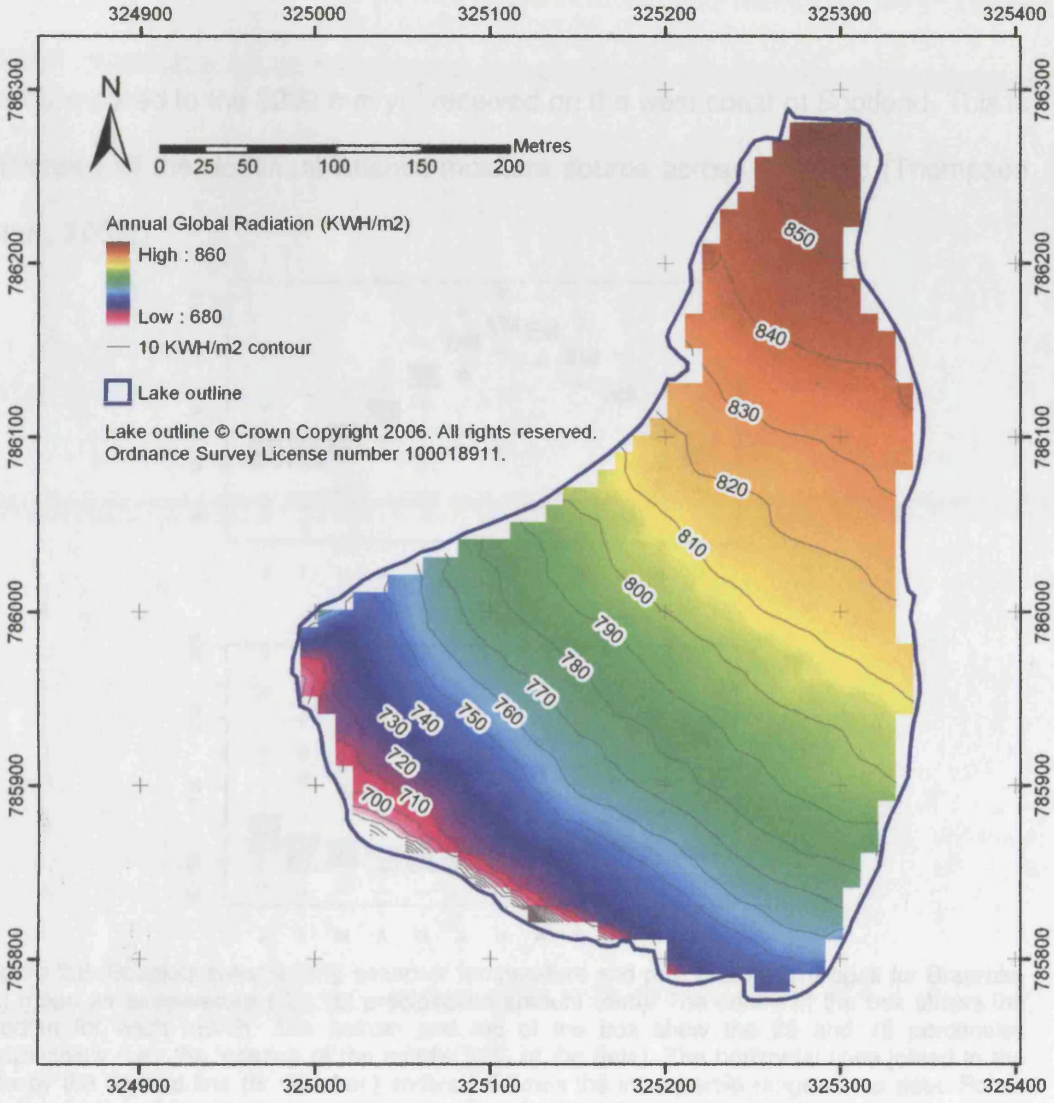

Figure 2.5: Light distribution and shading on the Lochnagar surface (Hughes, 2007).

at 339 m asl (Thompson *et al.*, 2007). Temperatures for Braemar (Figure 2.6) range from maxima in July of ~ 12 °C and minima in December-February of ~1 °C. Precipitation demonstrates a weaker seasonal pattern, with maxima between October-January and minima between April-July (Thompson *et al.*, 2007). Lochnagar experiences annual precipitation of ~ 1000 mm yr^{-1} which is relatively

low compared to the 2200 mm yr^{-1} received on the west coast of Scotland. This is indicative of the dominant Atlantic moisture source across Scotland (Thompson *et al.*, 2007).

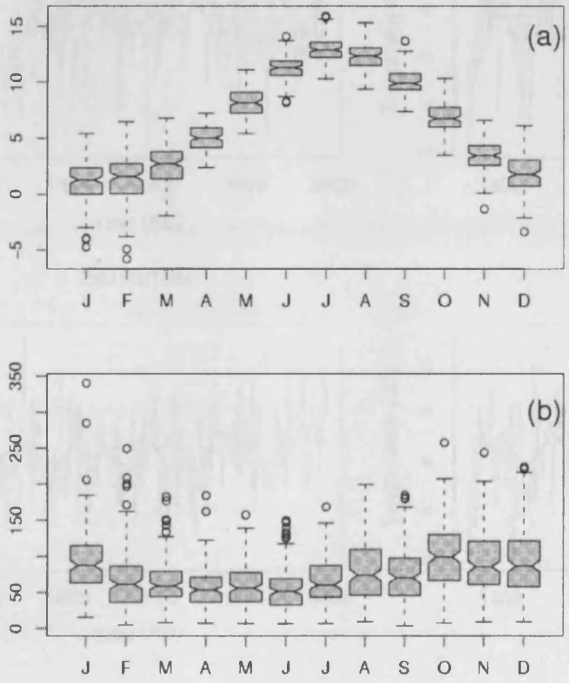

Figure 2.6: Boxplots summarising seasonal temperature and precipitation averages for Braemar, (a) mean air temperature (°C), (b) precipitation amount (mm). The centre of the box shows the median for each month. The bottom and top of the box show the 25 and 75 percentiles respectively (i.e., the location of the middle 50% of the data). The horizontal lines joined to the box by the dashed line (or 'whisker') shows 1.5 times the interquartile range of the data. Points (outliers) beyond the whiskers are drawn individually (from Thompson *et al.*, 2007).

Air temperature changes for the last 225 years have been reconstructed for Lochnagar by extrapolation from long-term low altitude weather stations (Agusti-Panareda *et al.*, 2000; Agusti-Panareda and Thompson, 2002) (Figure 2.7). Following cold decades around the 1780s and 1810s, annual temperatures for Lochnagar were found to have generally warmed by +0.3 °C century $^{-1}$ in the 1800s and +0.5 °C century $^{-1}$ in the 1900s (Agusti-Panareda and Thompson, 2002; Thompson *et al.*, 2007).

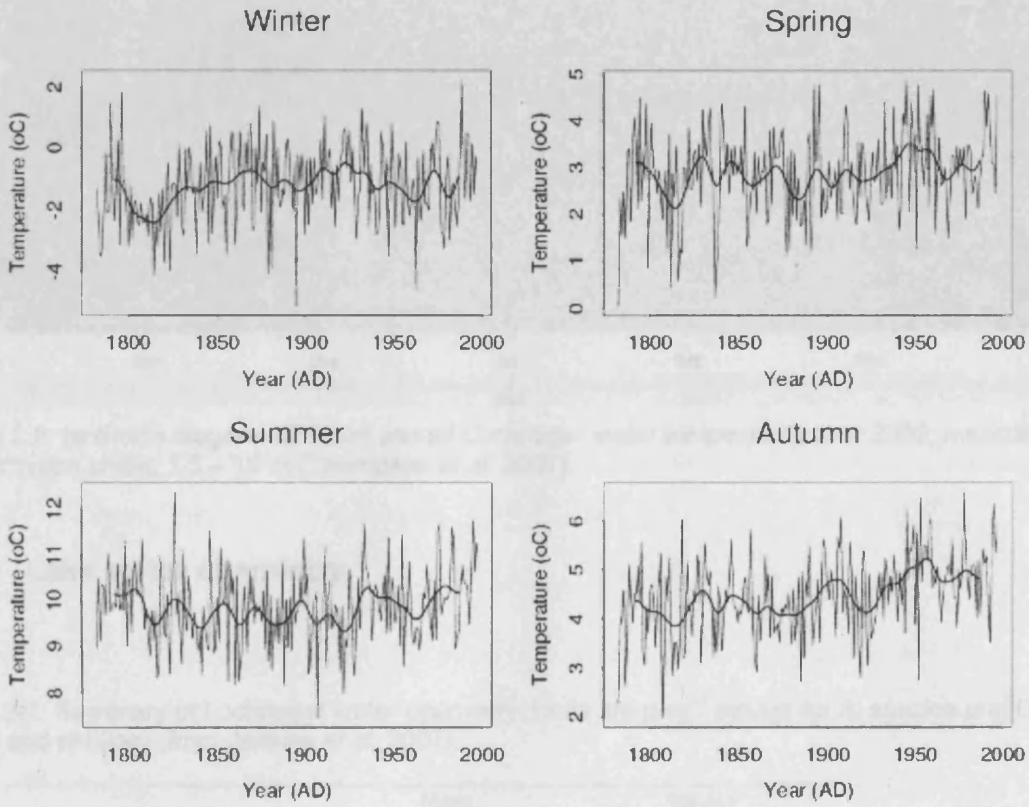

Figure 2.7: Air temperature hindcasts for Lochnagar (Thompson *et al.*, 2007).

2.2.4 Lake climate

Figure 2.8 illustrates the seasonal changes in the thermal profile of Lochnagar, demonstrating a clear pattern of seasonal stratification and mixing (for methods see 3.1.1). These data are described in more detail in Chapter 5 (Section 5.3.2) in the context of their effect on lake water oxygen isotope ratios. Essentially, lake water temperature at Lochnagar relates to a temporally smoothed response to daily air temperature (Kettle *et al.*, 2004; Thompson *et al.*, 2007).

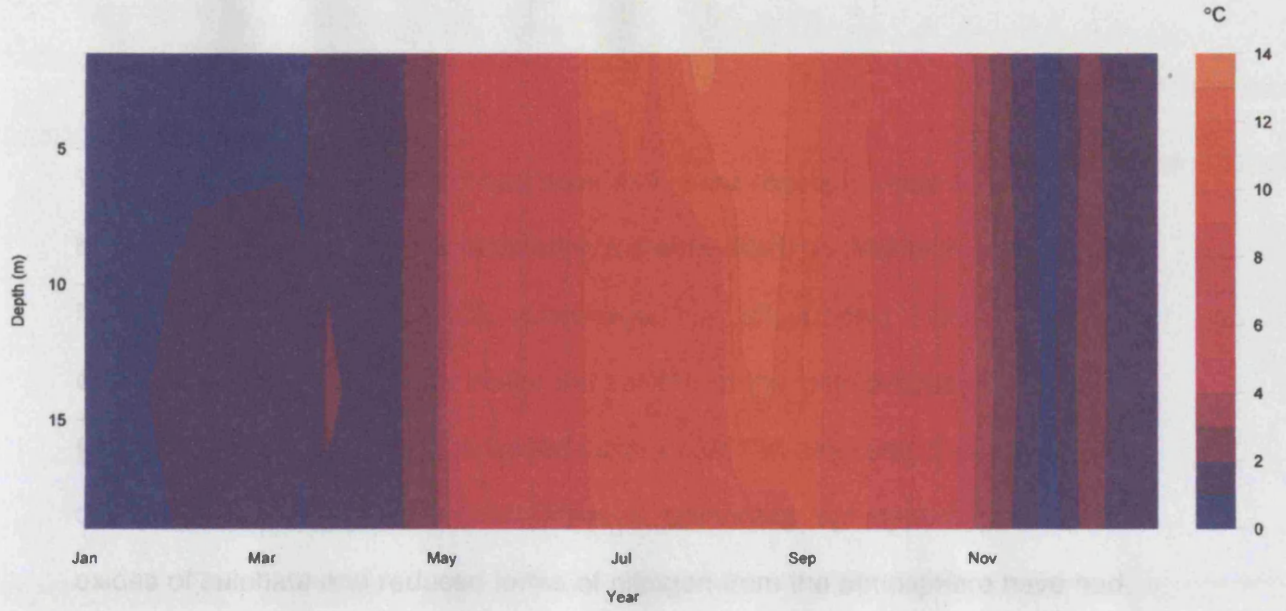

Figure 2.8: Isotherm diagram of mean annual Lochnagar water temperature over 2000, measured by thermistor chain, 1.5 – 19 m (Thompson *et al.* 2007).

2.2.5 Lake water chemistry

Table 2.1. Summary of Lochnagar water chemistry. Units are μeql^{-1} except for Al species and DOC (μgl^{-1}) and pH (log) (from Jenkins *et al.* 2007).

	Mean 4/2003-3/2004	Std.dev 4/2003-3/2004
pH	5.51	0.09
Acid Neutralising Capacity	5.87	1.23
Calcium	29.12	1.89
Magnesium	33.33	0.68
Sodium	84.78	4.35
Potassium	5.26	0.44
Total Soluble Aluminium	0.59	0.25
Soluble Labile Aluminium	0.31	0.09
Chloride	78.87	6.09
Sulphate	46.35	1.04
Non-seasalt Sulphate	38.07	0.51
Nitrate	22.04	2.65
Silica	74.64	11.96
Dissolved Organic Carbon	97.92	7.98

Water chemistry at Lochnagar has been monitored regularly since 1988 and the beginning of the Acid Waters Monitoring Network (AWMN) (Monteith *et al.*, 2001; Monteith and Evans, 2005). Lochnagar is oligotrophic, with chemical characteristics that reflect the major ion content of the local bedrock (Table 2.1) (Jenkins *et al.*, 2007). There is limited influence of sea-salt sodium and chloride, due to the distance from the coast, however historically high deposition levels of oxides of sulphate and reduced forms of nitrogen from the atmosphere have had a marked impact on lake waters (Jenkins *et al.*, 2001; 2007; Monteith *et al.*, 2007). Derived from industrial emissions which began during the industrial revolution in the mid-1800s, sulphur reached a peak during the early 1970s whereafter it has decreased sharply almost to background levels (Review Group on Acid Rain, 1990; Jenkins *et al.*, 2007). Nitrogen, however, reached a peak in the 1990s and there has been no appreciable decline to present day. The net effect of these deposits is to acidify the surface water, and Lochnagar has a low surface water mean pH of 5.5 (Table 2.1) (Jenkins *et al.* 2007). The seasonal pattern of lake water chemistry is described further in Chapter 6 (Section 6.3.4 and 6.3.5).

2.2.6 Freshwater ecology of Lochnagar

Typical of many high altitude, oligotrophic lakes, the aquatic flora of Lochnagar is characterised by a limited range of well adapted taxa. Light (1975) noted only two species of submerged aquatic macrophte – *Isoetes lacustris* and *Juncus*

bulbosus var. *fluitans*. These taxa remain the only macrophytes, however several bryophytes also exist, including *Sphagnum auriculatum* and the liverworts *Scapania undulata* and *Nardia compressa* (Flower *et al.*, 2007). Palaeolimnological investigations of aquatic pollen and macrofossils suggest that little change has occurred in the diversity of macrophytes at Lochnagar over recent timescales (Patrick *et al.*, 1989; Flower *et al.*, 2007). By contrast, the microflora – as indicated by fossil diatom and chrysophyte cyst analysis, and contemporary monitoring of epilithic diatoms and phytoplankton, has varied markedly over seasonal, inter-annual and inter-decadal timescales (Jones *et al.*, 1993; Rose *et al.*, 2004; Flower *et al.*, 2007; Monteith *et al.*, 2007).

Figure 2.9 illustrates monthly phytoplankton data collected by Evzen Stuchlik and colleagues between 1996-1998 (Flower *et al.* 2007). Despite a short and relatively intermittent sampling period, there are considerable similarities with other mountain lake communities (e.g. Felip *et al.*, 1999; Fott *et al.*, 1999; Pugnetti and Bettinetti, 1999; Brettum and Halvorsen, 2004). Chrysophytes (Chrysophyceae and Synurophyceae) dominated the phytoplankton biomass, in particular consisting of *Dinobryon cylindricum* Imhof, with additional contribution by spherical nanophytoplankton, blooms of *Oocystis* (Chlorophyceae), an unknown green flagellate, and the dinophyte *Wolozsynskia*. Phytoplankton assemblages and biomass demonstrated marked seasonality (Figure 2.9): Chrysophytes peaked in May during both 1997 and 1998; Chlorophyceae peaked in June throughout the mixed water column; cryptomonads (class

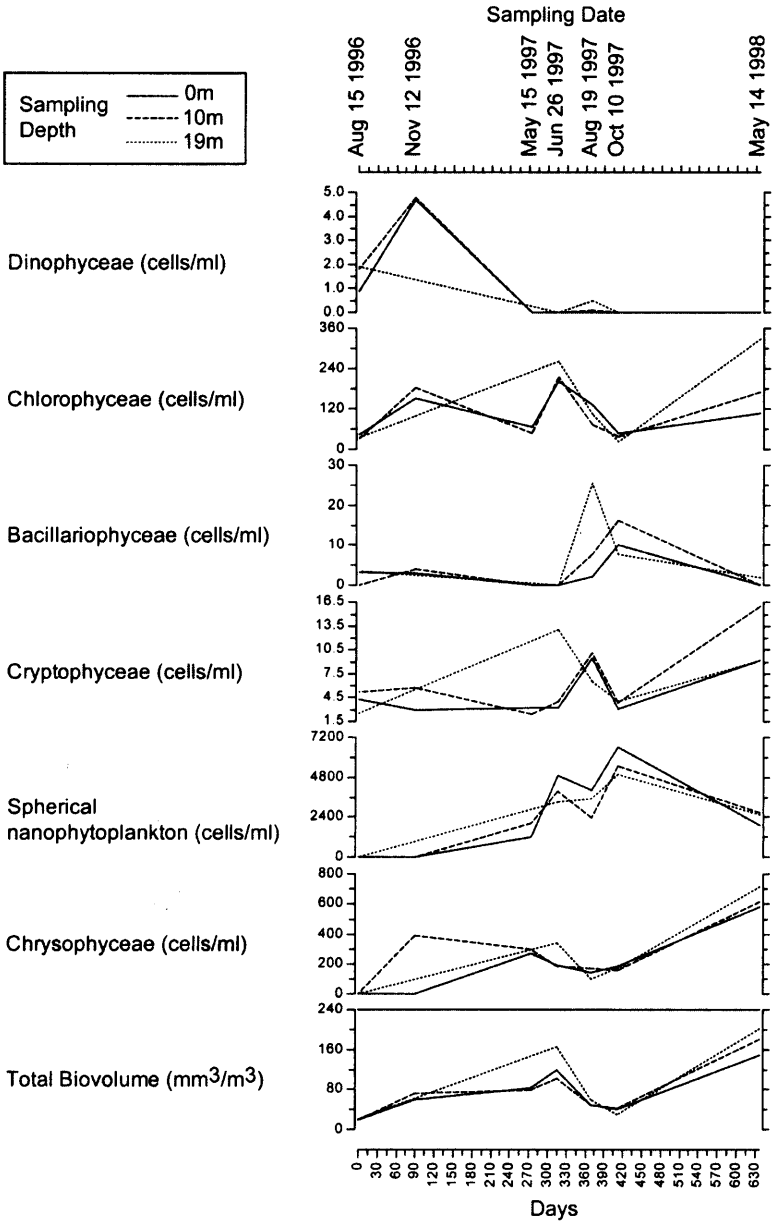

Figure 2.9: Lochnagar phytoplankton (data collected by Evzen Stuchlik, published by Flower et al. 2007).

Cryptophyceae, mainly *Cryptomonas* and *Rhodomonas*) bloomed in August followed by diatoms (class Bacillariophyceae, mainly *Aulacoseira*) in October. The abundances of spherical nanophytoplankton increased in June but generally showed a progressive rise towards an annual maximum in October.

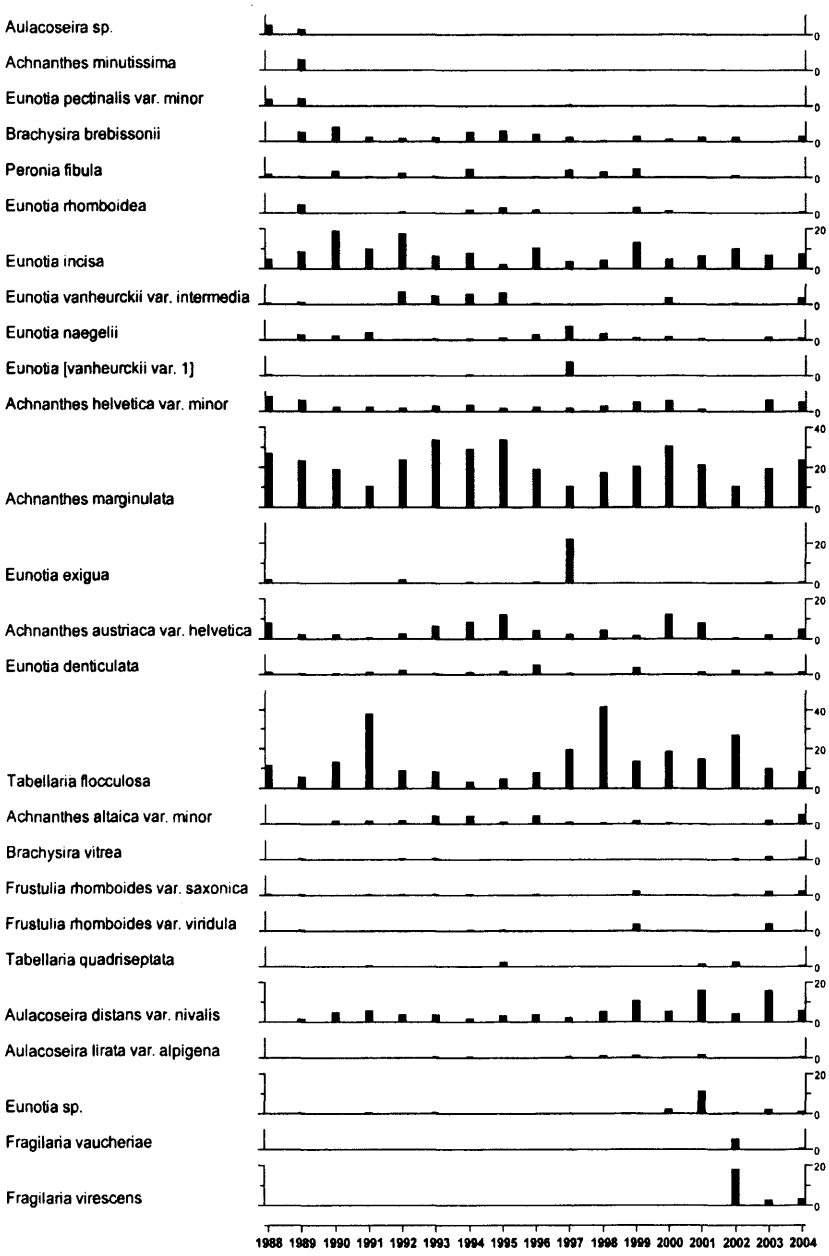

Figure 2.10: Epilithic diatom % relative abundance in annual samples at Lochnagar.

Cryptomonads, chrysophytes and diatoms preceded their surface water blooms by having high abundances in the hypolimnion, suggesting either incubation at depth or an earlier bloom not sampled (Flower *et al.* 2007).

In addition to phytoplankton, periphytic algal communities which live attached to substrates such as submerged plants (epiphyton), rocks (epilithon), sand grains (epipsammon) and within sediment biofilms (epipelon) play an important role in oligotrophic lake ecosystems. At Lochnagar, the majority of diatom taxa are benthic, with rock surfaces providing the dominant habitat (Flower *et al.* 2007). Epilithic diatoms have been sampled annually since 1988. Certain species, such as *Eunotia incisa*, *E. pectinalis* and *Brachysira brebissonii* have declined over the monitoring period while species such as *Aulacoseira distans* var. *nivalis* (which is both planktonic and benthic), *Fragilaria exiguiformis*, *F. vaucheriae* and *Tabellaria flocculosa* have tended to increase. Other species such as *Achnanthes marginulata*, *A. altiaca* var. *minor* and *A. helvetica* showed highest abundances during the middle of the sampling period (during the late 1990s) and others showed an increasing trend towards 2006 (*F. vaucheriae; Eunotia* spp.) or an irregular pattern through time (*E. exigua*) (Figure 2.10) (Flower *et al.* 2007). Seasonal observations regarding the abundance and taxonomic composition of epilithic diatoms at Lochnagar are described in Chapter 6 (Section 6.3.7.4).

Chapter 3:

Methods

3.1 Primary data

3.1.1 Meteorology and limnology

This thesis uses data collected as part of ongoing monitoring at Lochnagar by other researchers. Section 3.1.10 credits those responsible for collection of Lochnagar monitoring data. However where specifically relevant to this thesis, their methods are outlined in the following sections.

Lakeside air temperature, windspeed, relative humidity and rainfall amount was measured by an automatic weather station (AWS) at Lochnagar from 30 August 1996 to present (Rose, 2001). The AWS and all sensors used at Lochnagar were made or supplied by Delta-T Devices of Cambridge, U.K. Data were logged on a Delta-T DL2e logger. The AWS is powered by solar panels, and problems with power shortage and electrical faults have resulted in periods of missing data over the sampling duration. Lake water temperature was measured by automated thermistors at 1200GMT daily from 1 December 1999 to present, taking measurements at depths of 0.1 m, 1.5 m, 2.5 m, 3.5 m, 4.5 m, 6 m, 7 m, 9 m, 14 m and 19 m. Lake ice cover, catchment snow cover and snow depth were estimated by eye at two week intervals. Lake water samples were also collected from the lake

outflow stream every two weeks for analysis of major element chemistry at the Macaulay Institute for Land Use Research, Aberdeen and the FRS Freshwater Laboratory, Pitlochry.

3.1.2 Field sampling of meteoric waters for isotope analysis

Precipitation samples were collected at the lake side of Lochnagar using a total deposition collector (Figure 3.1) every two weeks from 21 January 2001 to 19 September 2005, except for periods where the site was inaccessible due to extreme weather, where the precipitation collector was frozen or when there was no rain since the previous collection. Silicone oil was used in the collector to prevent post-depositional evaporation of water. The collector was modified on 28 August 2004 with the addition of foam insulation in order to reduce freezing of waters and build up of algae inside the clear plastic tube.

Samples of snow were taken when the opportunity arose from fresh deposits on the surrounding terrain. In addition, water was sampled from an inflow spring rising at the southern lake margin (beginning 26 October 2000) and from the outflow stream – representing lake surface values (beginning 1 December 1999) (Figure 3.2). All samples for isotope analysis were collected in acid-washed air-tight polyethylene bottles and sealed with electrical tape.

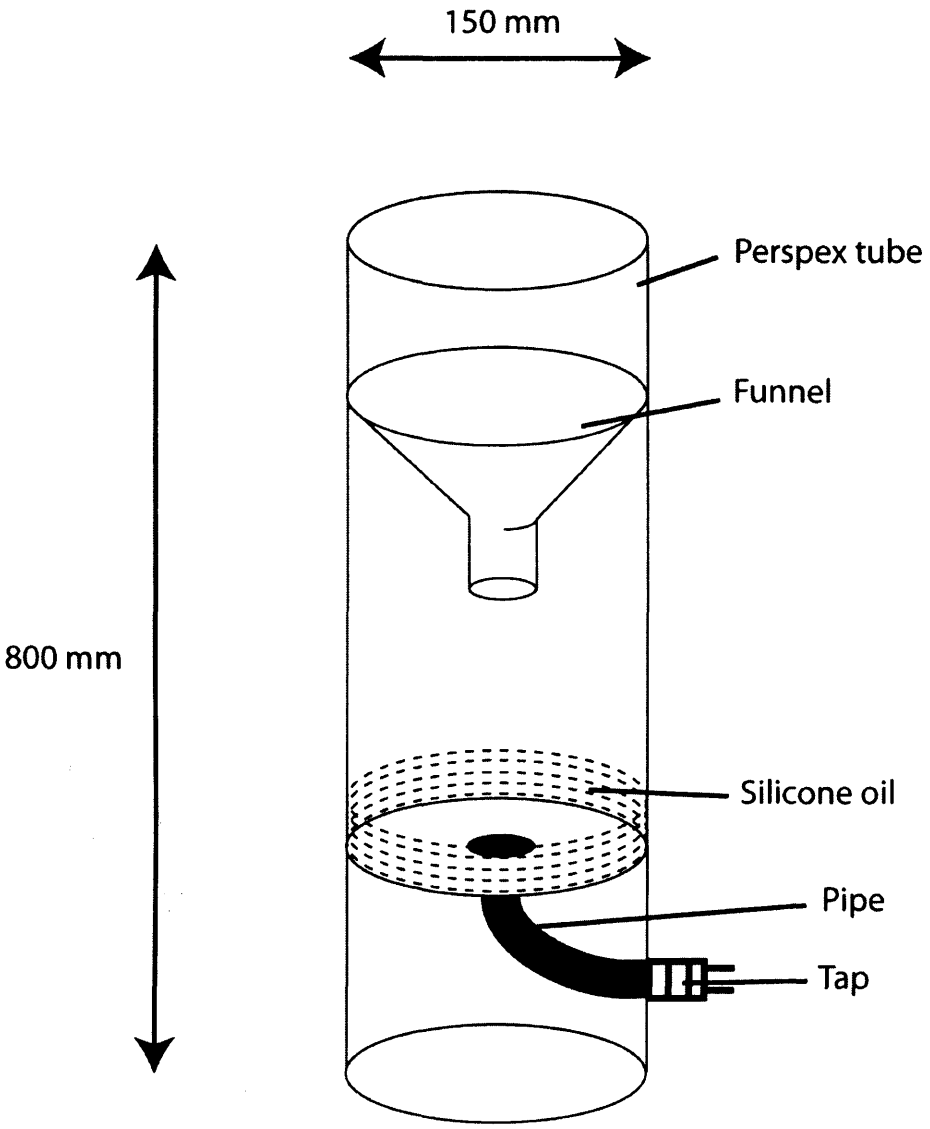

Figure 3.1: Illustration of total deposition rain water collector

3.1.3 Laboratory methods for isotope analysis of meteoric waters

Hydrogen for D/H isotope analysis was generated from unfiltered water samples by Zn reduction at 500°C between 21 January 2001 and 23 October 2003. Thereafter this method was superseded by Cr reduction from 5 November 2003

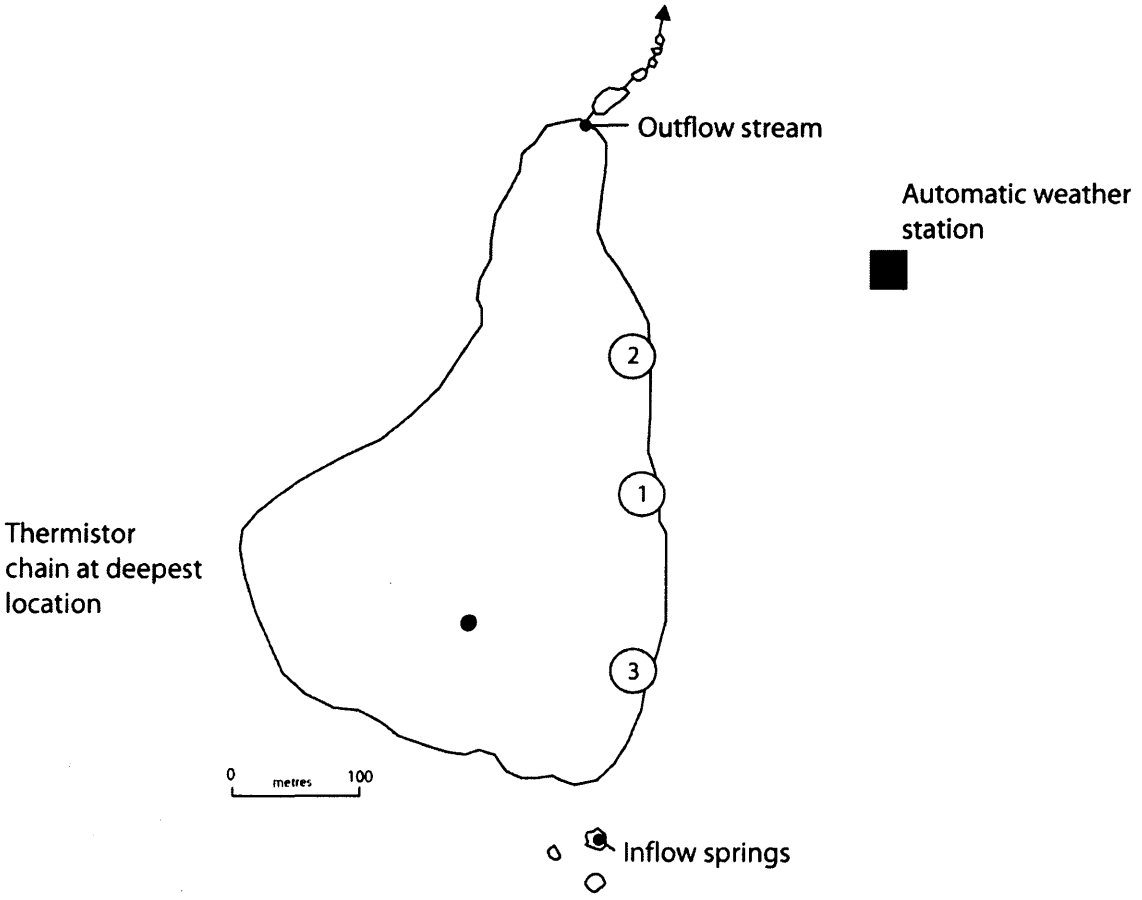

Figure 3.2: Map of Lochnagar catchment indicating sampling locations for inflow and outflow waters, location of thermistor chain within the lake and the location of the automatic weather station (AWS) relative to the lake shoreline. Water samples for isotope analysis of precipitation were sampled at the AWS. Numbered circles indicate the location of the diatom epilithon sampling sites. Site 1 was the site for sampling of bulk diatom material using artificial substrata for oxygen isotope analysis of diatom silica.

to 19 September 2005. For $^{18}O/^{16}O$ analysis, water samples were equilibrated with CO_2 using an ISOPREP 18 device. Mass spectrometry was performed on a VG SIRA (Zn δ^2H and $\delta^{18}O$) and Micromass IsoPrime (Cr δ^2H) in conjunction with laboratory standards calibrated against NBS standards at the NERC Isotope Geosciences Laboratory (NIGL), UK. Results are reported in the usual δ notation in per mille (‰) versus V-SMOW (see Section 1.2, Equation 1). Analytical errors are estimated as 0.05‰ for $\delta^{18}O$, 2‰ for δ^2H (Zn) and 1‰ for δ^2H (Cr).

3.1.4 Field sampling for chlorophyll-*a*, diatom cell density and taxonomic analyses

In order to track seasonal patterns in diatom cell density upon natural substrata, natural rock surface and littoral pelagic habitats were sampled monthly, weather conditions and access permitting. The following field samples were taken:

1) 2 litres of littoral lake water filtered onto Whatman GFC filter paper, treated with $MgCO_3$ and transported in a self-seal plastic bag for chlorophyll-*a* analysis of suspended matter.

2) From three submerged boulders, forming regular sampling sites, 6 quantitative epilithon samples were taken using a specialised epilithon sampler (Figure 3.3) (Flower, 1985) giving a total of 18 samples in ideal circumstances. The sampler was firmly pressed against the rock surface at 30 cm water depth, and the internal brush rotated at least 10 times to disturb the attached algae. Filtered water was then sucked through the chamber into two 60 ml syringes, removing all suspended algae. The resulting suspension was then subdivided into two for chlorophyll-*a* and taxonomic analyses. The volume of each sub-division was measured using the graduations on the syringe. The first sub-sample was filtered in the field onto a Whatman GFC filter paper and treated with a drop of $MgCO_3$ for chlorophyll-*a* analysis (Section 3.1.5.1). The second sample was transferred to a plastic sample bottle and treated with Lugol's Iodine prior to taxonomic analysis. Of

the 6 samples (taken at three sites), three were of natural standing biomass from here on referred to as 'old growth'. The other three samples at each site were made from the part of the boulder which had been cleaned 4 weeks earlier, in order to provide an indication of recent biomass accumulation ('new growth'). This surface was then thoroughly cleaned once more using a scrubbing brush.

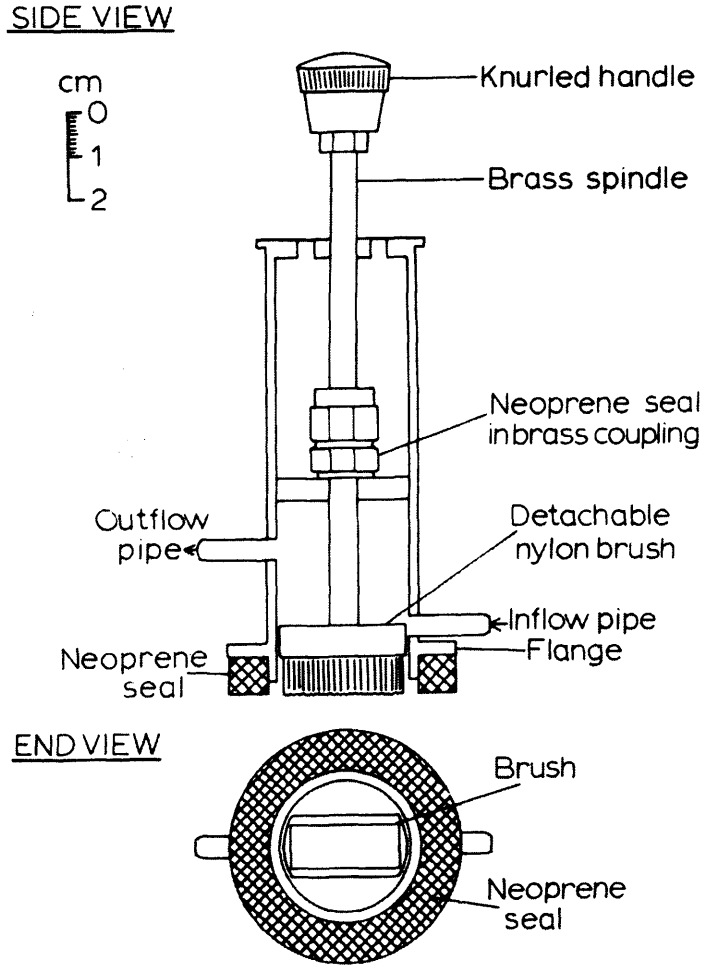

Figure 3.3: Illustration of diatom epilithon sampler (Flower, 1985).

3.1.5 Laboratory methods for chlorophyll-a, diatom cell density and taxonomic analyses

3.1.5.1 Chlorophyll-a

Following field sampling of suspended matter and epilithic algae (Section 3.1.4), filter papers were frozen within 24 hours of collection. Subsequent chlorophyll extraction was carried out as soon as possible. Frozen filter papers were ground in acetone, transferred to a graduated centrifuge tube and made up to 10 ml with acetone. Samples were centrifuged at 3000 r.p.m for 10 minutes and a sample of the supernantant transferred to a 1 cm^3 spectrophotometer cell. The absorbance of the extract was measured using a spectrophotometer at wavelengths 750 nm, 663 nm, 480 nm, 430 nm, and 410 nm. The value at 750 nm corrects for any fine colloidal matter and was subtracted from each of the other values. Chlorophyll concentration (C, µg/l) was calculated using the equation of Jeffrey and Humphrey (1975):

$$C = (11 \cdot A_{663} \cdot v) / V.d \qquad (5)$$

Where A_{663} is absorbance at 663 nm, v is the volume (in ml) of 90% acetone used for extraction, V is the volume of water filtered (in litres) and d is the path length (in cm) of the spectrophotometer cell (in this case 1 cm).

From this value, the concentration of chlorophyll-*a* (C_a) per unit surface area was calculated as:

$$C_a = ((C \cdot V) / f) / a \qquad (6)$$

Where *f* is the fraction of total epilithon sample filtered for chlorophyll analysis expressed as a proportion of 1 and a is the surface area sampled by the epilithon sampler in cm^2.

3.1.5.2 Diatom cell density and taxonomic analyses

Quantitative sub-samples of well mixed suspension, preserved in Lugol's Iodine, were taken and analysed in an Utermohl chamber under an inverted microscope at 500 x magnification (Wetzel and Likens, 2000). Diatom valves were enumerated at the genus level (using Cox, 1996) noting the presence or absence of chloroplasts as an indicator of live and dead cells. Other algal groups were identified and enumerated at the family level (using Canter-Lund and Lund, 1995; John *et al.*, 2003). Individual cells were counted where these could be distinguished, and filamentous colonies were recorded according to filament length.

3.1.5.3 Diatom slide preparation and taxonomic analyses

Further sub-samples were taken and prepared using standard techniques for diatom analysis (Battarbee *et al.*, 2001). Organic matter was removed by digestion in hot hydrogen peroxide and rinsed in distilled water three times in beakers, allowing the diatoms to settle out overnight prior to each decantation. Subsequent diatom material was transferred to centrifuge tubes and permanent slides were made using Naphrax. Diatoms were counted using oil immersion microscopy at 1200 x magnification and identified using the floras of Krammer and Lange-Bertalot (1986; 1988; 1991a; 1991b) and Camburn and Charles (2000). *Achnanthes* taxa were identified according to Flower and Jones (1989).

3.1.6 Field sampling of contemporary diatom silica for oxygen isotope analysis

Because the majority of diatom growth in Lochnagar is periphytic (Flower *et al.*, 2007, Chapter 2 - Section 2.2.6) collection of diatoms from the water column alone was deemed insufficient. Previous attempts at collecting seasonal diatom growth using a sequencing sediment trap resulted in samples too small for isotope analysis (Viv Jones pers. comm.) and in addition, sediment trap samples are more likely to be contaminated by re-worked diatoms from littoral deposits and surface sediments (Cameron, 1995). In order to collect fresh periphytic diatom matter in sufficient volume for preparation and analysis of oxygen isotopes, large surface area artificial

substrata were designed and deployed. The substrates (Figure 3.4) consisted of polypropylene sheets of dimension 1000 x 600 x 1 mm, attached to ropes with galvanised iron clips and suspended vertically in the water column between two subsurface buoys and two anchors. Four substrates were deployed, providing a total surface area of 4.8 m^2 for diatom colonisation. The substrates were deployed for 28 days prior to retrieval, which was achieved from the near-shore using an extendable boat hook and with the operator wearing chest-waders. On retrieval, the substrates were carefully detached from the ropes and placed into new plastic refuse sacks for transport to the laboratory. Clean substrates were attached to the ropes and the substrata re-deployed. Following the initial deployment, the artificial substrates were cut into 12 more manageable 600 x 333 mm sections.

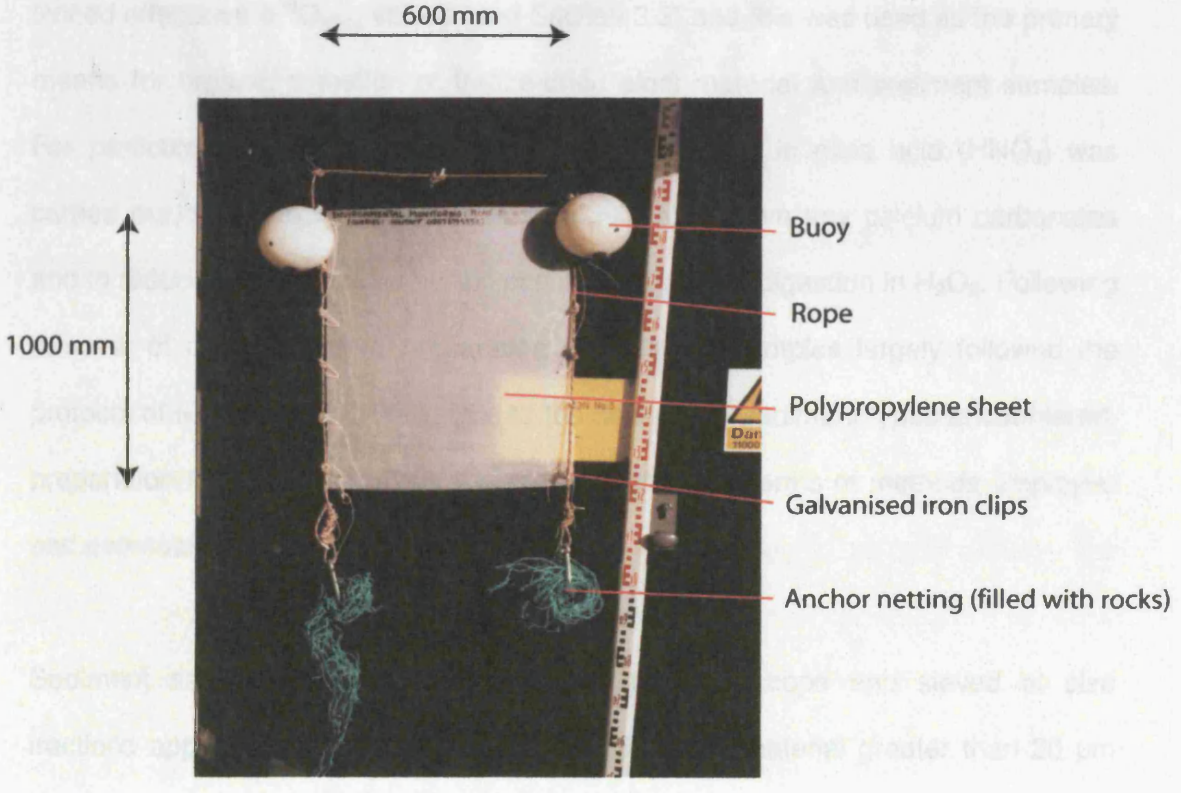

Figure 3.4: Annotated photograph of an artificial substrate.

In the laboratory, artificial substrate samples were frozen and freeze-dried in order to enable easy removal of algal material. Using a new toothbrush, algal matter was scrubbed from the substrates and rinsed with deionised water into a large acid-washed vessel. The resulting suspension was concentrated by centrifugation and freeze-dried for storage. Prior to re-deployment, all artificial substrata were thoroughly cleaned, acid washed and well rinsed in deionised water.

3.1.7 Preparation of material for oxygen isotope analysis of biogenic silica

Digestion in H_2O_2 is the most effective method for removal of organic matter, with limited effects on $\delta^{18}O_{silica}$ values (see Section 3.3) and this was used as the primary means for organic digestion of freeze-dried algal material and sediment samples. For particularly organic rich samples, further digestion in nitric acid (HNO_3) was carried out, followed by treatment in 50% HCl to remove any calcium carbonates and to reduce any iron oxides which can build up during digestion in H_2O_2. Following removal of organic matter, preparation of sediment samples largely followed the protocol of Morley *et al.* (2004). Due to the diversity of sediment types encountered, preparation for isotope analysis varied considerably in terms of methods employed and eventual success.

Sediment samples were analysed under light microscope and sieved at size fractions appropriate to that sample (usually isolating material greater than 20 µm but often >38 µm and on occasions > 75 µm). Following sieving, samples were

transferred to a centrifuge tube with deionised water and centrifuged, allowing the differential settling speed of diatoms and silt grains to separate the two (Morley *et al.* 2004). The diatom layer was carefully removed using a pipette and transferred to a separate vessel. Samples were further cleaned using repeated treatment in the heavy liquid sodium polytungstate (SPT). Samples were centrifuged over SPT with progressively lower specific density (2.3, 2.2, 2.1, 2.0 and 1.8) until a pure sample of biogenic silica was retrieved with a specific density between 1.8 and 2. For particularly contaminated samples, SPLITT flow fractionation was attempted (following Rings *et al.*, 2004; Leng and Barker, 2006) but to no beneficial outcome.

The final sample was rinsed in deionised water and vacuum filtered at 10 µm with an abundance of water to remove remaining traces of SPT. Although much of the cleaned material had dimensions smaller than 10 µm, the rapid accumulation of particles upon the sieve cloth under pressure has the effect of preventing fine grade particles from passing through the sieve cloth (Phil Barker pers. comm.) as verified by subsequent microscopic examination. The final material was carefully rinsed from the sieve cloth and transferred into a plastic storage vial. Samples were dried in air at 40°C prior to isotope analysis. Due to the small sample volume, and generally small (<10 µm) diatom size, sieving was deemed unsuitable in the preparation of the modern samples collected using artificial substrata from Lochnagar. In this case, only the SPT stage was used, with repeated treatments eventually yielding pure biogenic silica.

3.1.8 Analysis of oxygen isotopes in biogenic silica

Biogenic silica samples were prepared for oxygen isotope analysis following Haimson and Knauth (1983), Thorleifson (1984) and Matheney and Knauth (1989), using a fluorination line based on Clayton and Mayeda (1963) with BrF_5 as the fluorinating compound (Leng and Sloane submitted). Biogenic silica is reacted in three steps within a pure nickel reaction vessel, followed by oxygen extraction in two phases.

Initially, outgassing (dehydration) is performed to remove surficial and loosely bonded water in the reaction tubes at room temperature. A prefluorination step is then carried out, using a stoichiometric deficiency of BrF_5 at a low temperature (250°C) for 6 minutes to remove hydroxyl and loosely bound water in the sample. Following these preliminary steps, a full reaction is carried out at 450°C for ~12 hours in a pure nickel reaction vessel with an excess of reagent to dissociate O_2 from the silica. Bi-products, including SiF_4 and BrF_3 are condensed within the reaction vessel and two further traps by cooling the vessel with liquid nitrogen, thus liberating pure oxygen. O_2 is converted to CO_2 on a heated graphite rod and collected in a glass vessel (Clayton and Mayeda 1963). The CO_2 yield is calculated using a calibrated capacitance manometer. Oxygen yields were monitored in comparison with the calculated theoretical yield for SiO_2, with Quaternary and recent diatom samples typically yielding 70-80% of their theoretical oxygen yield, suggesting that between 20-30% of the oxygen is removed during prefluorination as

hydroxyl and loosely bonded water (both OH^- and H_2O) (Leng and Sloane submitted). $^{18}O/^{16}O$ ratios were measured on a Finnigan MAT 253 isotope ratio mass spectrometer (IRMS), and normalized using laboratory standards calibrated against the IAEA standard NBS28. Data are presented in the δ form, as per mille (‰) deviations from V-SMOW (Chapter 1, Section 1.2, Equation 1). A random selection of samples was analysed in duplicate to calculate within run and between run reproducibility. The standard laboratory diatomite control (BFC_{mod}) has a long term reproducibility of 0.3‰.

3.1.9 'Spiking' biogenic silica samples for oxygen isotope analysis

In some cases, diatom silica samples were 'spiked' with a known quantity of quartz standard (NBS28) in order to derive samples large enough for analysis (for discussion and method development see below, Section 3.4). The oxygen isotope composition of pure diatom silica was calculated as follows: The fraction of diatom silica (f_D), residual after pre-fluorination and hence influential to the final $\delta^{18}O_{silica}$ value, was calculated as:

$$f_D = \frac{f_T\left(W_D + W_Q\right) - f_Q W_Q}{W_D} \qquad (1)$$

where f_T is the measured total oxygen yield expressed as a fraction of the total initial sample (i.e. the residual silica fraction following pre-fluorination) and f_Q is the

residual fraction of quartz silica following pre-fluorination, assumed to equal 0.97 following extensive replicate analyses (H. Sloane pers. comm.). W is the weight in mg of quartz (W_Q) and diatom silica (W_D) comprising the initial sample. The absolute masses of quartz (Q) and diatom (D) silica for the final mixture, following pre-fluorination, were estimated as:

$$Q = f_Q W_Q \tag{2}$$

$$D = f_D W_D \tag{3}$$

and finally, the isotope composition of pure diatom silica (δ_D) was estimated as:

$$\delta_D = \frac{\delta_T (D+Q) - Q\delta_Q}{D} \tag{4}$$

where δ_T and δ_Q are the $\delta^{18}O_{silica}$ values for the total mixture and quartz standard respectively.

3.1.10 Note on collection of primary data

Not all the sampling regimes were initiated or managed by the author. Monitoring of Lochnagar thermal regime was initiated and managed by Don Monteith on behalf of the Acid Waters Monitoring Network (AWMN). This programme is also responsible for the regular sampling of lake water for chemical analyses. Meteorological monitoring using the automatic weather station and monitoring of catchment snow and lake ice cover was initiated and managed by Neil Rose, with observations made by Jo Porter. Sampling of waters for isotope analysis was carried out by Jo Porter and initiated by Melanie Leng. Isotope analysis of water samples from Lochnagar was carried out at NERC Isotope Geosciences Laboratory (NIGL) by Carol Arrowsmith. All other sampling at Lochnagar concerning diatom ecology and isotope geochemistry was carried out and managed by the author. The author performed all preparation work prior to isotope analysis of biogenic silica, however analytical work was carried out by Hilary Sloane at NIGL. All other primary data presented in this thesis, including laboratory measurements, preparation, experimental work and taxonomic analyses are the result of work carried out by the author.

3.2 Secondary Data

In addition to primary data, this thesis uses secondary data from a variety of sources:

Table 3.1: Summary of secondary data sources.

Data	Collected by	Source
Isotopes in precipitation at Valentia (Eire)	International Atomic Energy Agency, Vienna, Austria.	IAEA/WMO (2004) Global Network of Isotopes in Precipitation. http://isohis.iaea.org
Isotopes in precipitation at Wallingford (United Kingdom)	Groundwater Systems and Water Quality Programme. British Geological Survey, Wallingford, Oxfordshire, U.K	IAEA/WMO (2004) Global Network of Isotopes in Precipitation. http://isohis.iaea.org
Isotopes in precipitation at Keyworth (United Kingdom)	British Geological Survey, Wallingford, Oxfordshire, U.K.	IAEA/WMO (2004) Global Network of Isotopes in Precipitation. http://isohis.iaea.org
Meteorological data for Balmoral, Braemar, Wallingford, Keyworth, Nottingham and Central England Temperature	UK Met. office	British Atmospheric Data Centre (BADC) http://badc.nerc.ac.uk/home/
Jenkinson indices	Hadley Centre for Climate Prediction and Research	Hadley Centre for Climate Prediction and Research

Data	Collected by	Source
Meteorological data for European sites including Valentia		European Climate Assessment Dataset http://eca.knmi.nl/
North Atlantic Oscillation Index		Climatic Research Unit (CRU), University of East Anglia http://www.cru.uea.ac.uk/cru/data/nao.htm
Spatial estimates for isotopes in precipitation	Estimates using formula of Bowen and Ravenough (2003)	www.waterisotopes.org
Bi-weekly water chemistry data for Lochnagar	Fisheries Research Services (FRS), Pitlochry, Scotland	Fisheries Research Services (FRS), Pitlochry, Scotland
Bi-weekly water chemistry data for Lochnagar	Macaulay Land Use Research Institute, Aberdeen, Scotland	Macaulay Land Use Research Institute, Aberdeen, Scotland
European lake limnological and meteorological data	D. Sachse and others, Max Planck Institute for Biogeoscience, Jena, Germany.	Sachse *et al.* (2004)

3.3 Method development

Despite the use of oxygen isotope ratios in biogenic silica as a palaeoclimate proxy for over three decades (i.e. since Labeyrie, 1974), a number of methodological issues have yet to be addressed and some preparation approaches still require standardisation. Consequently, an aspect of method development is necessary in order to improve the application of oxygen isotope ratios of biogenic silica to

palaeoclimate research. In the following sections, details are given of two experiments designed to establish appropriate means of removing organic matter from sediment samples prior to biogenic silica separation (Section 3.3.1; Tyler *et al.*, 2007) and to test the applicability of 'spiking' biogenic silica samples, i.e. mixing the biogenic silica sample with a known mass of quartz silica prior to analysis, in order to enable analysis of samples otherwise too small for standard procedure (Section 3.3.2).

3.3.1 Method development (1): Testing the effects of organic removal procedures on the integrity of $\delta^{18}O$ measurements from biogenic silica.

The importance of mineral contamination effects on $\delta^{18}O_{silica}$ measurements has been highlighted by a number of recent publications (Morley *et al.*, 2004; 2005; Rings *et al.*, 2004; Lamb *et al.*, 2007). However, little attention has been paid to the organic material in diatom samples – in particular, the effects of the many procedures used to remove organic matter prior to analyses. In order to determine the effectiveness of organic matter removal methods and their influence on $\delta^{18}O_{silica}$, simultaneous experiments were carried out on two different types of lake sediment (Tyler *et al.*, 2007). Organic rich material from Lochnagar (NAG) was used to determine the loss of organic matter with each treatment. A laboratory standard diatomite (KFC), which contains virtually no organic material (<0.2%), was subjected to the same organic removal methods in order to assess the effects on the integrity of $\delta^{18}O$ measurements. Ideally, identical material should have been used in both

experiments, however this is problematic since $\delta^{18}O_{silica}$ can not be determined until all organic matter has been removed due to the formation of organo-fluorine compounds when organic matter is reacted with fluorine based reagents. It is therefore impossible to identify the isotope value independent of any chemical treatment.

3.3.1.1 Methods

Eleven treatments are summarised in Table 3.2. For each treatment, samples were prepared in triplicate. Both sediment types (NAG and KFC) were treated identically throughout. All samples were weighed before and after treatment, chemically treated sediments were dried at 70°C prior to weighing. The first five methods involved digestion in H_2O_2 (treatments 1-2) or HNO_3 (treatments 4-5), washing three times in deionised water and treatment in 50% HCl for 2 hours at 70°C to remove traces of calcium carbonate. Treatment 3 was identical to treatment 1, using H_2O_2 for 30 hours, but with the HCl step omitted, in order to account for any independent effects of HCl. Treatment 6 used aqua-regia ($HNO_3/HClO_4$), a highly reactive mixture of HNO_3, HCl and water, which has also been used in standard hot digestion (Shemesh *et al.*, 1995; 2001; Rosqvist *et al.*, 2004). Microwave digestion following the procedure of Parr et al. (2004) was tested as a means to accelerate the treatment process. The sample and aqua-regia were heated and pressurised to 30psi for 8 minutes in Teflon microwave vessels with a ramp up time of 4 minutes. Samples were allowed to cool to air temperature, before washing in deionised water.

Treatments 7 and 8 were carried out using a laboratory furnace, with temperatures and treatment times based on standard procedures for calculation of organic matter and carbonate content by loss on ignition (Dean, 1974). Treatments 9 and 10 were carried out in a specially built vacuum furnace comprising a thermostatically controlled element wrapped around a glass cylinder and attached to a rotary pump (Gilg *et al.*, 2004). The samples were allowed to react at lower temperatures (250°C and 450°C) for 60 minutes. A range of treatment temperatures and times have previously been used to remove organic carbon from biogenic carbonates (e.g. Shackleton *et al.*, 1983; Carpenter and Lohmann, 1995; Spero *et al.*, 1997). The conditions chosen represent a high and low temperature average. More recently, the consensus appears to be not to pretreat biogenic carbonate samples by heating due to the marked effect this has on the carbonate mineralogy, even at temperatures of 100°C (Gaffey *et al.*, 1991; Dickson, 2001). Treatment 11 used a Nanotech Plasmaprep P100 furnace set at standard settings, ie. oxygen pressure of 5 psi, flow rate 50%, chamber pressure of 1 mB and temperature of 150°C. The samples were combusted in ceramic crucibles and cooled in a desiccating bell-jar.

Table 3.2: The eleven treatments used in the organic removal experiment.

Treatment	Method	Time (minutes)	Temperature (°C)
1	H_2O_2, followed by HCl	1800	70
2	H_2O_2, followed by HCl	3600	70
3	H_2O_2, no HCl	1800	70
4	HNO_3, followed by HCl	1800	70
5	HNO_3, followed by HCl	3600	70
6	Aqua-regia ($HNO_3/HClO_4$) in microwave	12	-
7	Ignition in air	130	550
8	Ignition in air	180	950
9	Ignition in vacuum (4mB)	60	250
10	Ignition in vacuum (4mB)	60	450
11	Ignition in plasma furnace (1mB)	960	150

Percentage organic carbon (%TOC) analyses of NAG material were performed by combustion in a Carlo Erba 1500 at the NERC Isotope Geosciences Laboratory, Nottingham. Samples containing about 1 milligram of carbon were loaded in tin capsules and dropped, through a continuous helium flow, into a 1020°C furnace. A pulse of oxygen gas promotes oxidation at >1400°C. Product gases (CO_2, N_2, H_2O, SO_2) were further oxidised by chromium oxide and silvered cobaltous oxides, with sulphur compounds removed on the silver. Excess O_2 was removed by passage into a 650°C furnace containing elemental copper, which also reduces any nitrogen oxides to N_2, and water is removed by passage through magnesium perchlorate. The CO_2 and N_2 remaining in the He stream were separated through a GC column and gas concentrations measured by thermal conductivity. The samples were calibrated against an Acetanilide standard. Replicate analysis of well-mixed samples indicated a precision of $<\pm 0.1\%$.

Treatments 1-11 were also applied to the standard pure diatomite (KFC). These samples were then analysed for oxygen isotope ratios (see Section 3.1.8 for analytical methodology).

3.3.1.2 Results

Stage 1: Effectiveness of organic removal of the eleven treatments (Figure 3.5a, Table 3.3)

- Digestion in H_2O_2 for 30 and 60 hours followed by HCl (treatments 1 and 2) was extremely effective at removing organic matter, leaving minimal (0-0.1%) residual carbon. Samples undergoing treatment 3 were not analysed for TOC.
- Digestion in HNO_3 (treatments 4 and 5) failed to remove all organic matter, although digestion for 60 hours removed more organic matter (0.2-0.3% residual) than digestion for 30 hours (0.3-0.5%).
- Microwave digestion (treatment 6) was less effective at removing organic matter than the other chemical methods (1.3-1.6% residual), but as the treatment lasted only 12 minutes (following the published procedure of Parr et al., 2004) this was the most efficient treatment in terms of organic removal over time.
- Ignition in air (treatments 7 and 8) was most effective, removing 100% of organic carbon, and there is apparently no additional benefit of ignition at 950°C over 550°C.

- Heating under vacuum (treatment 9 and 10) failed to remove the organic matter, although heating at 450°C removed more organic matter (0.9% residual) than at 250°C (5.6% residual).
- Plasma ashing (treatment 11) failed to remove all organic matter (2.7% residual), despite a much longer preparation time than the other heating methods.

Stage 2: The effects of the organic removal treatment on $\delta^{18}O_{silica}$ (Figure 3.5b, Table 3.3)

- Digestion in H_2O_2 (treatments 1 and 2) resulted in a slight increase in $\delta^{18}O_{silica}$ values by 0.25‰, but within the error margins of values for untreated material (±0.3‰). There is very little difference between material treated for 30 and 60 hours except for a small increase over time, which may be insignificant as it is within error. Values of $\delta^{18}O_{silica}$ for treatment 3, where the HCl step was omitted, were the same as for treatment 2, suggesting that HCl has no additional effect on $\delta^{18}O_{silica}$.
- Treatments 4 (HNO_3 for 30 hours), 5 (HNO_3 for 60 hours), 6 (microwave and aqua-regia), 7 (ignition at 550°C) and 11 (plasma ashing) resulted in no significant change in $\delta^{18}O_{silica}$ values.
- Ignition at 950°C (treatment 8) resulted in markedly lower $\delta^{18}O_{silica}$ by around 5‰. This treatment had the most significant effect on $\delta^{18}O_{silica}$ and may be connected with a change in silica structure. However, heating under vacuum

at 250°C and 450°C (treatments 9 and 10) resulted in higher mean $\delta^{18}O_{silica}$ values (27.7 and 27.4‰), and both produced results which did not show good reproduction (with sd of 0.7 and 0.5‰).

Table 3.3: Mean $\delta^{18}O_{silica}$ values for treated and untreated KFC and total organic carbon (%TOC) for treated and untreated NAG material. σ = 1 standard deviation from mean of n values.

Treatment	$\delta^{18}O_{silica}$ (‰)	σ	n	TOC (%)	σ	n
NONE	26.5	0.3	5	7.5	0.5	3
1	26.8	0.4	3	0.1	0.0	3
2	26.9	0.4	3	0.0	0.0	3
3	26.7	0.2	2			
4	26.6	0.3	2	0.4	0.1	3
5	26.7	0.0	3	0.2	0.0	3
6	26.5	0.3	3	1.5	0.2	3
7	26.5	0.1	3	0.0	0.0	3
8	22.0	0.8	3	0.0	0.0	3
9	27.3	0.7	3	5.6	1.0	3
10	27.4	0.5	3	0.9	0.5	3
11	26.5	0.2	3	2.7	0.2	3

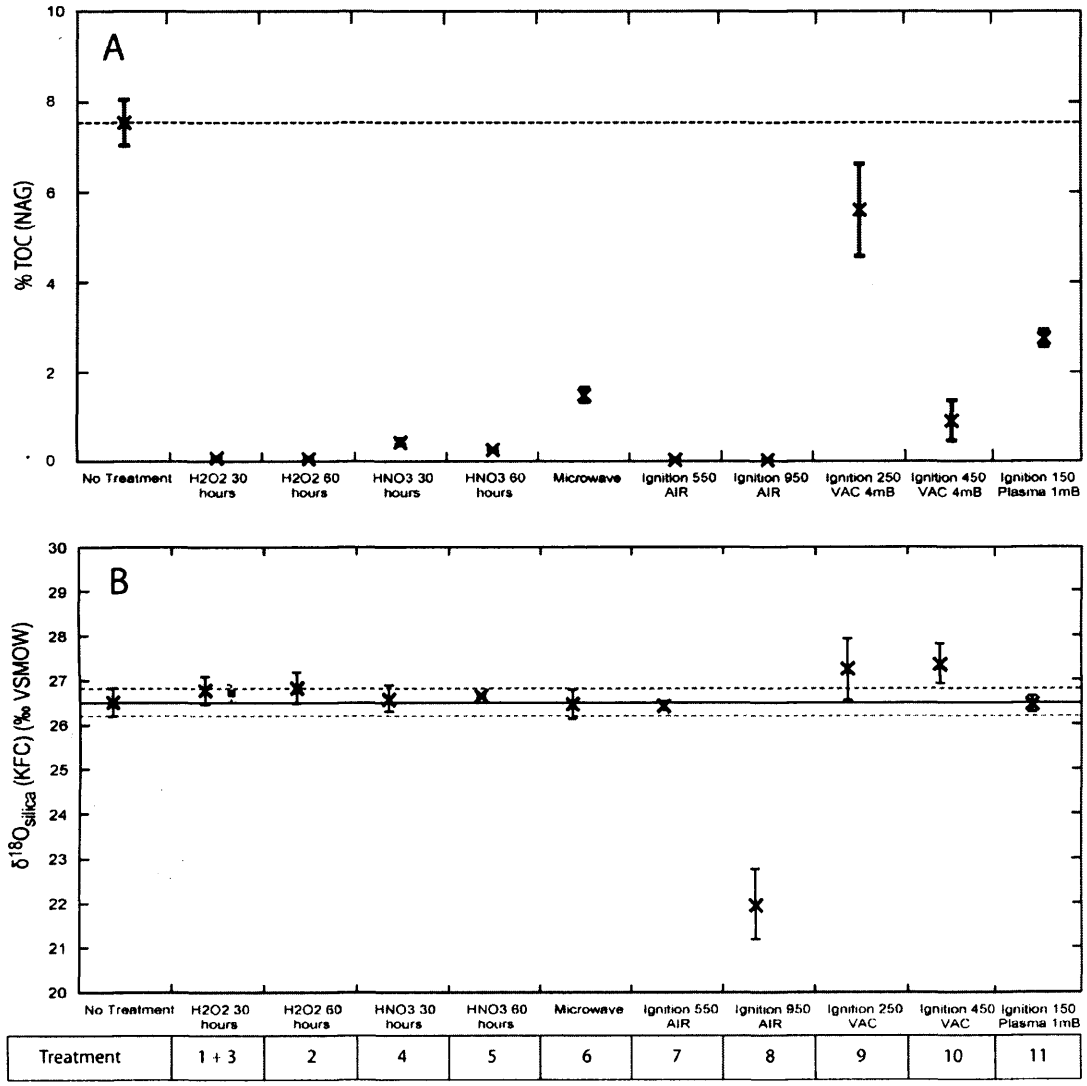

Figure 3.5: a): Organic matter concentration in NAG sediment before and after treatments, expressed as % Total Organic Carbon (TOC). Error bars represent one standard deviation (n=3). Dashed line represents mean %TOC for untreated NAG sediment (n=5). b): Effects of organic matter removal on $\delta^{18}O_{silica}$: comparing values for KFC material before and after treatment. $\delta^{18}O_{silica}$ values for KFC diatomite expressed are means of triplicate analyses. Horizontal solid and dotted lines represent mean and plus/minus one standard deviation of untreated KFC to enable comparison with treated material. Error bars represent one standard deviation.

3.3.1.2 Discussion

Of the procedures tested, ignition in air at 550°C was the quickest and simplest method. The treatment effectively removed organic matter and it did not affect $\delta^{18}O_{silica}$ values. To the detriment, however, the NAG sediment partially solidified in the furnace, which would hinder sieving and settling - both common methods subsequently used when isolating pure biogenic silica (e.g. Morley, et al. 2004). Digestion in H_2O_2 was effective at removing organic material, yet slightly increased $\delta^{18}O_{silica}$ values after both 30 and 60 hours treatment. Since the offset created by H_2O_2 digestion was within analytical error for repeated measurements of untreated material (±0.3‰), it is unclear whether this effect is significant or not. The minor increase in deviation with time, however, suggests that it is possible that the negative effects of H_2O_2 treatment may be mediated by reducing the reaction time. It would appear that the HCl treatment is not responsible for the observed isotope offset following treatments 1 and 2.

Of the other methods tested, HNO_3 digestion (treatments 4 and 5) had little effect on $\delta^{18}O_{silica}$ values but failed to fully remove all organic material. A slight trend towards decreasing organic carbon with time suggests that the method may be more effective with longer digestion times, higher temperatures or more frequent replacement of the reagent. Similarly, though microwave assisted digestion in aqua-regia failed to remove all organic material, the treatment only lasted 12 minutes and there is potential for improvement.

As expected, heating under vacuum was ineffective at removing organic matter although significantly more was removed at the higher temperature. In addition there was modification of the $\delta^{18}O_{silica}$ values at both 250°C and 450°C. Plasma ashing at 150°C was also ineffective at removing organic matter but had no effect on $\delta^{18}O_{silica}$. Ignition in air at 950°C removed all organic matter, but no more effectively than ignition at 550°C, and resulted in a marked decrease in $\delta^{18}O_{silica}$. At these temperatures, the KFC diatomite fused to become solid crystals, thus making the material unsuitable for subsequent cleaning techniques, and probably represents structural changes in the silica.

3.3.1.3 Summary: The effects of organic removal treatments on $\delta^{18}O_{silica}$

Overall, the $\delta^{18}O_{silica}$ values demonstrated remarkable stability under a series of experiments representing extreme preparatory conditions. However it is clear that certain organic removal preparations are not suited to $\delta^{18}O_{silica}$ analysis. The data suggest that ignition in air at 550°C is the most effective procedure for removal of organic matter prior to isotope analysis of biogenic silica, although solidification may prove problematic with some types of sediment. Therefore overall the results suggest that H_2O_2 methods are the most effective treatment for removing organic matter, but reaction times should be kept to the minimum required.

3.3.2 Method development (2): Testing the effects of quartz spiking on oxygen isotope ratios of diatom silica

Diatom productivity and biomass are markedly seasonal (see Chapter 6). Diatom yields from artificial substrata from Lochnagar showed a similar pattern – with the greatest volumes (0.85-1.05 g, dry organic weight) sampled in September and October 2004 and March and April 2005. Unfortunately, samples collected during July and August in both years yielded very small diatom volumes (~0.1 g dry organic weight) (See Chapter 6 for further discussion). Organic contents in most cases accounted for ~80% of the total weight. In addition to the biogenic material attached to the artificial substrata, some allocthonous material had accumulated on the substrata – probably the result of local soil erosion to the lake. This contamination had to be physically removed prior to isotope analysis of pure biogenic silica, with the consequence that a number of the resultant samples became too small for standard analytical procedure.

In circumstances where samples are too small for routine oxygen isotope analysis, 'spiking' the sample with a known quantity of standard material has the potential of bringing the sample weight to a size suitable for analysis. To date, this approach has yet to be used for the analysis of oxygen isotope ratios from biogenic silica, however it was attempted because the small samples collected from Lochnagar prevented the use of standard practice in many cases. Samples were 'spiked' by mixing the diatom sample with quartz standard (NBS 28) with a very accurately known $\delta^{18}O$

value. The oxygen isotope ratio of pure diatom silica was then estimated by isotope mass balance calculations (Equations 1 – 4). In order to test the applicability of this approach, a pilot study was designed to investigate the effects of spiking on estimated diatom $\delta^{18}O_{silica}$.

3.3.2.1 Methods

Three samples were created, comprising mixtures of quartz standard and Lochnagar pure diatom silica, with differing quartz:diatom mixture ratios (~0.5, ~1 and ~2). The samples were analysed using standard procedure (above – Section 3.1.4) and the isotope composition of pure diatom silica estimated by mass balance (Equations 1 – 4). The estimated $\delta^{18}O_{silica}$ value was then compared with that of the pure diatom sample.

The sensitivity of the mass balance model to weighing error was tested by re-calculating estimated diatom $\delta^{18}O_{silica}$ values using a range of diatom silica weights, within the potential weighing error margins. This was carried out for each of the three samples analysed, enabling the effect of increasing quartz:diatom ratio on potential error generation to be observed.

3.3.2.2 Results

Total $\delta^{18}O_{silica}$ values (i.e. of quartz + diatom) decline with an increasing proportion of quartz silica, which has a relatively low $\delta^{18}O$ of +9.6‰ (Table 3.4; Figure 3.6). Estimated diatom $\delta^{18}O_{silica}$ values fall within the range of the analytical error of the control when the quartz:diatom ratio is small (0.5). However, where quartz:diatom ratios are >1, estimated diatom $\delta^{18}O_{silica}$ values were 1-1.5‰ too low. It is therefore evident that $\delta^{18}O_{silica}$ estimates achieved by spiking small samples should be treated with caution, especially when a mixture with a quartz:diatom ratio >1 is used.

Weighing error sensitivity tests (Figure 3.7) reveal an increasing range of potential error with increasing quartz:diatom ratio of the silica mixture. Where the quartz:diatom ratio is low (~0.5), a ±0.1 mg weighing error potentially causes a range of $\delta^{18}O_{silica}$ estimates ±0.25‰ with respect to the 'true' value. This is within recognised analytical error for mixed diatom assemblages (±0.3‰). Where the quartz:diatom ratio is increased to ~1 and ~2, the same weighing error leads to a potential range of ±0.6‰ and ±1.2‰, beyond analytical error.

Table 3.4: Details of experiment to test effects of spiking diatom silica for $\delta^{18}O_{silica}$ analysis. W_D and W_Q are initial weights of diatom and quartz silica, f_T, f_D and f_Q are residual fractions of total sample (T), diatom and silica quartz following the pre-fluorination step. D and Q are the calculated weights of diatom and quartz silica following pre-fluorination, and hence influencing the final $\delta^{18}O_{silica}$ value. δ_T, δ_Q and δ_D are the $\delta^{18}O_{silica}$ values of total sample and quartz (measured) and diatom silica (estimated). For further detail see Equations 1-4, Section 3.1.9.

W_D mg	W_Q mg	$W_Q:Q_D$	f_T (measured)	f_D (estimated)	f_Q (assumed)	D mg	Q mg	δ_T ‰	δ_Q ‰	δ_D ‰
2.05	4.42	2.2	0.82	0.51	0.97	1.05	4.29	13.7	9.6	30.4
2.99	3.18	1.1	0.77	0.56	0.97	1.67	3.08	16.8	9.6	30.0
4.17	2.03	0.5	0.79	0.69	0.97	2.88	1.97	22.5	9.6	31.2
Unspiked sample										31.4

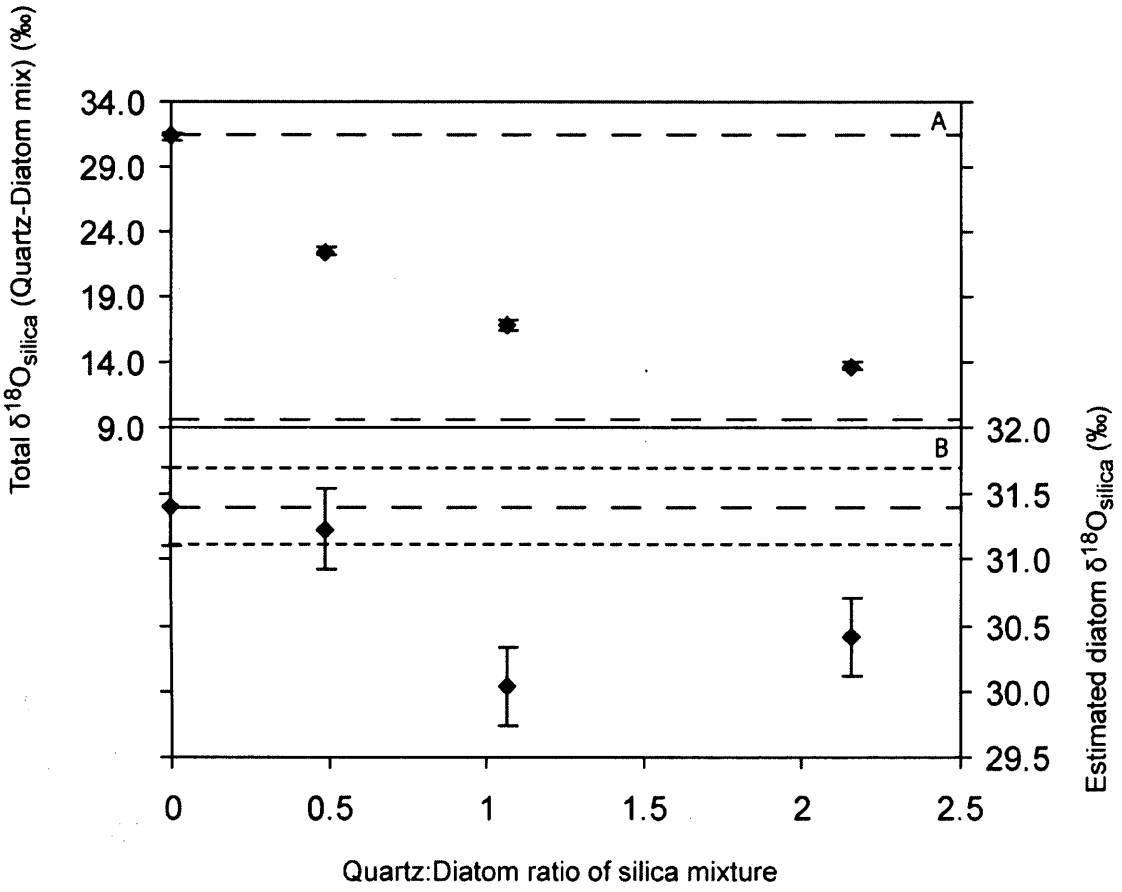

Figure 3.6: Effects of spiking biogenic silica with quartz on the un-mixed estimate of quartz-free silica. (A) $\delta^{18}O_{silica}$ values of quartz-diatom mixture; (B) Estimated $\delta^{18}O_{silica}$ of pure diatom biogenic silica, against quartz:diatom ratio in mixture. Dashed line = control (pure diatom standard). Dotted lines = range of analytical error of control.

3.3.2.3 Discussion

A number of methodological issues have been recently investigated with regards the treatment and analysis of diatom silica samples for oxygen isotope ratios (Morley *et al.*, 2004; Rings *et al.*, 2004; Lucke *et al.*, 2005; Lamb *et al.*, 2006; Tyler *et al.*, 2007). Here, experiments were carried out in order to test the applicability of 'spiking'

samples, to deal with the problem of insufficient sample sizes. The data suggest that spiking samples prior to oxygen isotope analysis of biogenic silica should be carried out with caution. Samples with quartz:diatom ratios >1 revealed marked offsets up to 1.5‰ lower than the control. This is most likely due to error in the estimation of the relative proportion of the two components in the mixture. With oxygen isotope analyses of diatom silica, this matter is complicated further by the pre-fluorination stage – whereby a stoichiometric deficiency of reagent is used to remove hydrous biogenic silica prior to the full reaction (Leng *et al.*, 2001). It was assumed that the mass of the quartz standard, which does not have a hydrous outer layer, undergoes a constant minor degradation (0.3%) during prefluorination – based on hundreds of replicate analyses (H. Sloane pers. comm.). The contribution of diatom silica to the total signal can therefore be estimated. For example, where the final oxygen yield for the diatom + quartz mixture = 80%, it was assumed that 20% of the initial diatom sample was removed in prefluorination. Consequently, errors in the weighing of diatom silica can result in errors in the final estimated $\delta^{18}O_{silica}$. Figure 3.7 illustrates how the sensitivity of spiked $\delta^{18}O_{silica}$ estimates to weighing error diminishes with a decrease in the proportion of quartz used. For quartz:diatom ratios of 0.5, weighing errors of ±0.1 mg (equivalent to long term reproducibility: H. Sloane, pers. comm.) lead to only minor $\delta^{18}O_{silica}$ errors of ±0.25 ‰, which is within the range of analytical reproducibility. However, when quartz:diatom ratio is increased to ~2, the same weighing error leads to a deviation of 1‰ (Figure 3.7). The most likely source of such error is incomplete desiccation of the silica sample prior to weighing. Usually, samples are air-dried in a cabinet at 40°C. For standard analyses, this approach is

considered sufficient, however diatom silica is extremely porous, and it is possible that even after prolonged air-drying, moisture remains within the silica pores. In addition, dry silica can absorb water vapour from the atmosphere during transfer for analysis. For a sample with a quartz:diatom ratio of ~2, 0.1 mg accounts for ~6% of the total weight of diatom silica. Water retention within the silica pores therefore has great potential for causing weighing error.

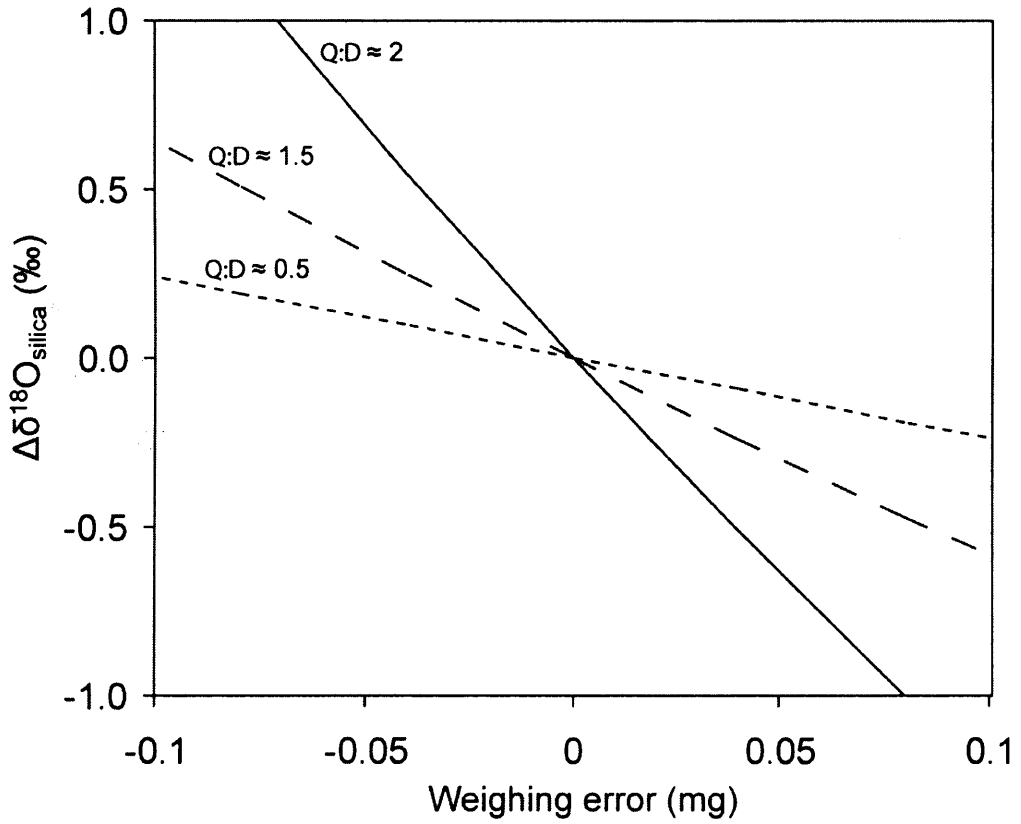

Figure 3.7: Sensitivity of spiked $\delta^{18}O_{silica}$ to weighing error. $\Delta\delta^{18}O_{silica}$ = change of $\delta^{18}O_{silica}$ in response to positive/negative weighing error. Q:D = ratio of quartz to diatom silica in spiked sample.

3.3.2.4 Summary: The effects of 'spiking' on $\delta^{18}O_{silica}$

'Spiking' samples with quartz:diatom ratios <1 appears to produce accurate estimates for pure diatom $\delta^{18}O_{silica}$ values. Spiking with quartz:diatom ratios >1 can lead to errors – most likely due to amplification of weighing error in the mass balance calculation. Therefore, at present there is a limit to the minimum size of diatom silica sample which can be analysed (~4 mg), however analysis of smaller samples may be possible if greater weighing precision and control over silica moisture content can be achieved.

Chapter 4:

Climate controls over oxygen isotope ratios of precipitation at Lochnagar, plus other sites in Great Britain and Ireland

4.1 Introduction

The initial link between climate change and the oxygen isotope composition of sedimentary diatom silica is the oxygen isotope composition of precipitation entering the lake, and the climatic factors which drive that signal (Chapter 1, Figure 1.1). Records of the isotopes of oxygen and hydrogen in past precipitation are commonly used as tracers of past climate change. In particular, isotope studies of snow and ice accumulation in polar and alpine regions - direct archives of palaeo-precipitation - have led to large scale advances in our understanding of past and present climate variability (Dansgaard 1964; Petit *et al.* 1999; Thompson *et al.* 2000; Stauffer *et al.* 2004). However, changes in the isotope composition of past precipitation can also be inferred from lake sediment deposits, tree ring cellulose, palaeo-groundwaters, and speleothems, subject to various degrees of modification (Edwards *et al.* 1996; Rozanski *et al.* 1997; von Grafenstein *et al.* 1999; Robertson *et al.* 2001; Teranes and McKenzie 2001; Rebetez *et al.* 2003; McDermott 2004; Danis *et al.* 2006). Such archives are

valuable because they offer a more geographically diverse perspective of past atmospheric isotope hydrology to complement ice core records.

In order to appreciate the effects of climate change on the diatom silica oxygen isotope record from Lochnagar, an understanding of the climatic controls over the oxygen isotope composition of precipitation is vital. Rain waters are the fundamental source of almost all lake waters. Even where surface processes greatly modify lake water isotope composition, or where the inflow of water into a lake is temporally smoothed via groundwater passage, changes in the isotope composition of rain waters can still have an important effect on long term lake water isotope composition. If the surface effects of evaporation are minimal, lake waters can directly reflect the isotope composition of rainfall and the meteorological information stored within that signal. The relationship between oxygen isotope ratios in precipitation and lake waters at Lochnagar is discussed in detail in Chapter 5. This chapter aims to investigate how changes in local and regional meteorological factors are manifest in the oxygen isotope composition of precipitation at Lochnagar. In order to obtain a broader perspective, three additional datasets from elsewhere in the British Isles are also analysed.

Theoretically, the controls over isotope ratios in precipitation are well established (Dansgaard 1964; Gedzelman and Arnold 1994; Gat 2000; Araguas-Araguas *et al.* 2000). Essentially, the oxygen isotope composition of precipitation (referred to as $\delta^{18}O_P$) reflects a process of rain-out of atmospheric moisture from the

evaporation source, predominantly the tropical ocean (Piexoto and Oort 1983) to the point of precipitation. As an air mass cools, precipitation is formed in isotopic equilibrium with atmospheric vapour. Isotope fractionation during raindrop formation can be explained as a process of Rayleigh distillation (Equation 1), whereby condensation is instantly removed from the cloud preventing further isotope exchange between precipitation and cloud water vapour (Dansgaard 1964).

$$d\delta = \varepsilon^* \left(1 + \frac{\delta}{10^3}\right) d \ln f \qquad (1)$$

where ε^* is the liquid-vapour fractionation factor at the ambient temperature and f the fraction of water in the air mass relative to its initial value at the evaporating source. Heavy isotope species are preferentially condensed during cooling, leading to enrichment of light isotopes in the water vapour as the air mass proceeds. Deviation from the Rayleigh model can occur due to further isotope exchange between liquid raindrops and water vapour beneath the cloud base, depending on the size and velocity of the raindrops and the isotope composition of the ambient atmospheric water vapour. In addition, evaporation of falling precipitation can lead to increased $\delta^{18}O_P$ relative to initial condensation (e.g. Friedman *et al.* 1992). Solid precipitation (snow and hail), however, does not readily exchange isotopes with ambient vapour and therefore tends to preserve the signal fixed during condensation (Facy *et al.* 1963; Dansgaard 1964; Jouzel *et al.* 1975).

At a particular location, air temperature and precipitation amount are important variables which determine $\delta^{18}O_P$ (Dansgaard 1964). Air temperature plays a fundamental role in forcing water condensation. In addition, air temperature is the principle control over the liquid-vapour equilibrium fractionation factor ε^* (Equation 1), determining the thermodynamic equilibrium between water vapour and condensate (Dansgaard 1964). In many cases, precipitation amount co-varies with the relative moisture depletion of an air mass between the evaporation source and site of condensation, and therefore affects $\delta^{18}O_P$ through the rain-out process (*f* in Equation 1). Precipitation amount can further affect $\delta^{18}O_P$ by indirectly influencing the degree of isotope re-equilibration between rain drops and water vapour beneath cloud-level, and the amount of evaporation of liquid precipitation (Dansgaard 1964). These so called temperature and precipitation amount 'effects' are supported by global correlations between weighted mean $\delta^{18}O_P$ and mean annual temperature and precipitation (Dansgaard 1964; Rozanski *et al.* 1993; Araguas-Araguas *et al.* 2000). However, application of spatial models to temporal isotope changes at specific locations is increasingly regarded as problematic (Noone and Simmonds 2002; Treble *et al.* 2005), not least because the smoothed spatial correlation between $\delta^{18}O_P$, temperature and latitude, reflecting the global rain-out process, obscures a great deal of the local variability in moisture sources and atmospheric circulation. The source of moisture formation and the trajectory of the air mass prior to arriving at the site of interest can have a marked effect on the initial isotope composition of atmospheric vapour and on the cooling and rain-out history of the air mass

(Friedman *et al.* 2002a). Consequently, it is difficult to apply empirical models based on global climate-$\delta^{18}O_P$ relationships to data from specific locations (Heathcote and Lloyd 1986; Noone and Simmonds 2002). Studies of $\delta^{18}O_P$ time series reveal variable correlations with precipitation and temperature, depending on the temporal monitoring resolution and the effects of meteorological processes such as air-mass mixing, air flow direction and variable rain forming processes (Heathcote and Lloyd 1986; Lawrence and Gedzelman 1996; Lawrence *et al.* 1998; Friedman *et al.* 2002b; Noone and Simmonds 2002; Darling and Talbot 2003; Celle-Jeanton *et al.* 2004; Yamanaka *et al.* 2004; Treble *et al.* 2005; Liebminger *et al.* 2006). In general, it is too simple to assume that all of the variance in $\delta^{18}O_P$ at a particular site can be interpreted in terms of a single forcing agent such as air temperature or precipitation amount, yet this approach prevails in palaeoclimate research. In an island setting, such as the British Isles, the location of the site with regard to aspect and distance from the coastline and direction of oncoming weather are likely to play an important role in mediating the isotope response to climate forcing (Darling and Talbot 2003).

The stable isotopic composition of rainfall in the British Isles, and the relationships between $\delta^{18}O_P$ and temperature and precipitation amount have previously been described in detail by Darling and Talbot (2003). They conclude that although some climatic information can be gleaned from $\delta^{18}O_P$, much remains to be quantified concerning the controls over monthly $\delta^{18}O_P$. In this chapter, new data from Lochnagar are presented, and a broader approach is

taken by incorporating atmospheric circulation indices in the analysis. The circulation indices offer a quantitative account of the direction, force and character of the weather patterns over the British Isles, and their effects are assessed alongside local air temperature and precipitation records using multivariate statistical methods. The aim is to develop improved empirical models which explain monthly $\delta^{18}O_P$ patterns. This multivariate approach is also applied to previously published monthly monitoring data from Wallingford, Oxfordshire (1984-2000), Valentia, County Kerry, Eire (1984-2000) and Keyworth, Nottinghamshire (1988-1996) in order to develop the findings of Darling and Talbot (2003).

The atmospheric circulation indices used are based on the Jenkinson dataset (Jenkinson and Collinson 1977; Jones *et al.* 1993; Kilsby *et al.* 1998; Wilby 1998; Phillips and McGregor 2001) which describe synoptic scale wind flow over the British Isles. Previously, these indices have been successfully used in studying regional precipitation amount patterns (Kilsby *et al.* 1998; Phillips and McGregor 2001) and they can potentially play a valuable role in downscaling general circulation model output to understand regional climate change (Conway and Jones 1998).

4.2 Data manipulation and analytical methods

4.2.1 Data sources and manipulation

Isotope monitoring data for Wallingford, Keyworth and Valentia (Figure 4.1) consist of monthly rainwater samples, collected on the 15th of each month and accumulated since the 15th of the previous month. These data are supplemented by temperature and precipitation measurements taken at the monitoring station. At Keyworth, temperature was not measured from 1984-1988 and data from the nearby Nottingham weather station is used instead. Table 4.1, Chapter 3, Section 3.2, summarises all secondary data sources used in this thesis. Isotope samples from Lochnagar were collected every 14 days (Chapter 3). However in order to aid comparison between sites, the average monthly $\delta^{18}O_P$ was calculated. This approach is not without potential set-backs: in some cases, monthly data represent the mean of three samples, whereas in other cases, it represents just one. Inevitably, an unknown portion of the water included in one month fell in the preceding month. In addition, it would have been preferable to calculate the weighted mean $\delta^{18}O_P$ from the bi-weekly samples. Meteorological data from the Lochnagar automatic weather station (AWS) is intermittent, however, and to rely solely on weighted mean $\delta^{18}O_P$ would have led to a marked reduction in the number of data points available. For the purpose of statistical analyses of monthly $\delta^{18}O_P$ data for Lochnagar, mean monthly air temperature and precipitation amount was interpolated from the nearby Balmoral station. Figure

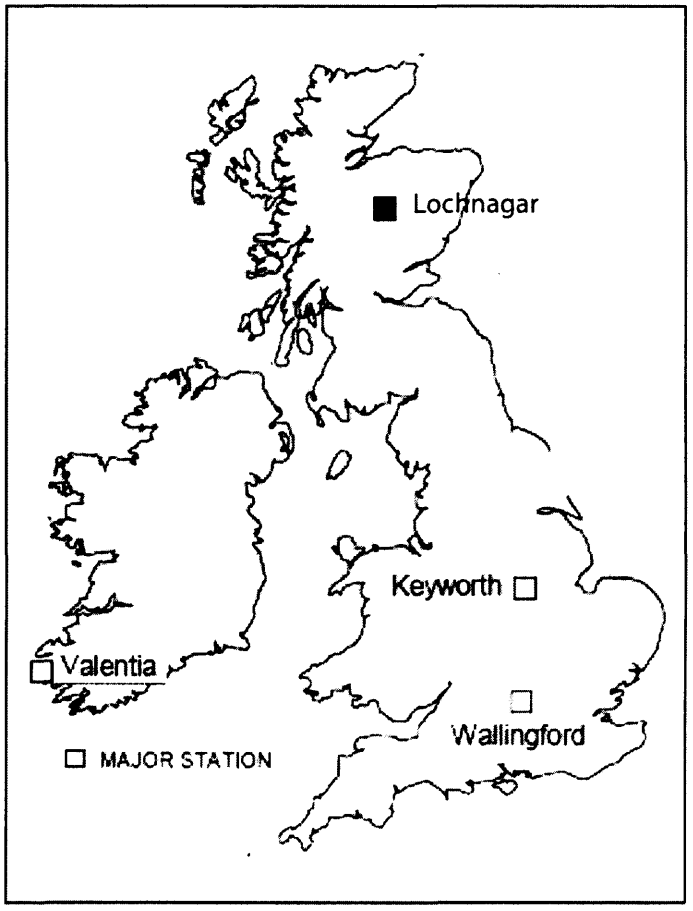

Figure 4.1: Site locations for study of isotopes in precipitation. Modified from Darling and Talbot (2003).

4.2 illustrates the correlation between monthly temperature and precipitation for the two weather stations. The correlation between precipitation amount at Balmoral and Lochnagar decreases dramatically when the temporal resolution is increased from monthly data, and consequently this approach was deemed unsuitable for weighting the bi-weekly $\delta^{18}O_P$ for Lochnagar. Comparison between weighted monthly $\delta^{18}O_P$ from Lochnagar, where Lochnagar precipitation data are available, and the arithmetic mean monthly $\delta^{18}O_P$ reveals very little difference in

Table 4.1. Detail of atmospheric circulation indices and their calculation where p_n = mean sea level pressure at grid point n (Figure 4.3) following Jenkinson and Collinson (1977). * ZW and ZS not used in subsequent analyses.

Abbreviation	Index	Calculated as
PM	Mean sea level pressure (hPa)	$PM = \frac{1}{n}(p_1 + ... + p_n)$
FW	Westerly flow	$FW = \frac{1}{2}(p_{12} + p_{13}) - (p_4 + p_5)$
FS	Southerly wind flow	$FS = 1.74\left[\frac{1}{4}(p_5 + 2*p_9 + p_{13}) - \frac{1}{4}(p_4 + 2*p_8 + p_{12})\right]$
F	Resultant wind force	$F = (FW^2 + FS^2)^{1/2}$
D	Resultant wind direction	D = arctan(FW/FS) if $FS < 0$ D = arctan(FW/FS) + 180 if $FS > 0$
ZW*	Westerly shear vorticity	$ZW = 1.07\left[\frac{1}{2}(p_{15}p_{16})\frac{1}{2}(p_8 + p_{12})\right] - 0.95\left[\frac{1}{2}(p_8 + p_9) - \frac{1}{2}(p_1 + p_2)\right]$
ZS*	Southerly shear vorticity	$ZS = 1.52\left[\frac{1}{4}(p_6 + 2*p_{10} + p_{14}) - \frac{1}{4}(p_5 + 2*p_9 + p_{13}) - \frac{1}{4}(p_4 + 2*p_8 + p_{12}) + \frac{1}{4}(p_3 + 2*p_7 + p_{11})\right]$
Z	Total shear vorticity	$Z = ZW + ZS$
N, NE, E, SE, S, SW, W, NW	Frequency of days per month characterised by flow direction	e.g. NE = 1 if 22.5°< D <67.5° E = 1 if 67.5°< D <112.5°

the two – suggesting a lack of significant repetitive pattern in intra-monthly precipitation amounts. Temperature and precipitation amount are expressed as the monthly mean of daily mean (temperature) and daily total (precipitation) values for the $\delta^{18}O_P$ sampling period. In the case of precipitation amount, this removes the problem of absolute rainfall being greater for months with 31 days. Mean monthly temperature data are irrespective of days with or without precipitation, and are not weighted according to precipitation amount.

Variability in the direction, velocity and vorticity of the atmospheric flow were quantified using circulation indices (the Jenkinson dataset) which cover the whole British Isles region (Jones *et al.* 1993; Kilsby *et al.* 1998; Wilby 1998; Phillips and McGregor 2001). Daily parameters are calculated from an algebraic combination of 1200 GMT mean sea-level pressure at regularly spaced grid points (Figure 4.3) with calculations summarised in Table 4.1 (Jenkinson and Collinson 1977). Using the wind direction index (*D*), 8 flow direction indices were derived as dummy variables, according to the occurrence or otherwise of daily weather being characterised by each particular wind direction, for example, daily NE = 1 if *D* falls within the range 22.5°-67.5°. All vorticity and flow units are geostrophic and expressed as hPa per 10° latitude at 55° North (Jones *et al.* 1993). For comparison with monthly isotope data, the arithmetic mean of all flow indices was calculated, except for the directional dummy variables (N, NE, E, SE, S, SW, W, NW) for which the monthly sum was calculated, giving the frequency, for each month, of days characterised by a particular wind direction.

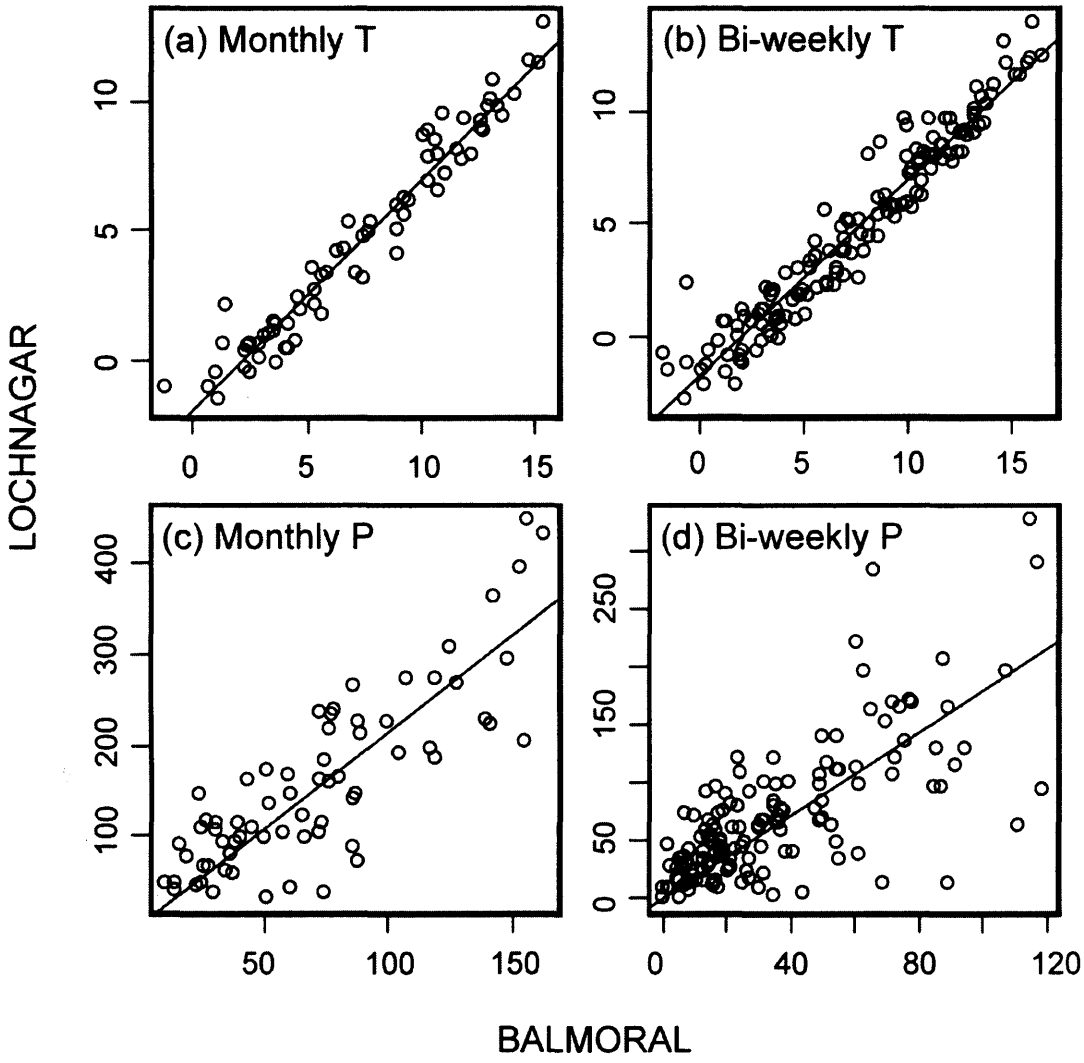

Figure 4.2. Comparison of monthly and bi-weekly air temperature (T, °C) and precipitation amount (P, mm) for Balmoral (x axes) and Lochnagar (y axes). Solid lines represent the linear best fit. For precipitation amounts, the best fit intercept was fixed at zero. (a) Monthly mean air temperatures: $y = 0.87x - 1.86$, $R^2 = 0.95$; (b) Bi-weekly mean air temperatures: $y = 0.87x - 1.81$, $R^2 = 0.93$; (c) Monthly total precipitation amounts: $y = 2.14x$, $R^2 = 0.68$; (d) Bi-weekly precipitation amounts: $y = 1.79x$, $R^2 = 0.48$.

Monthly values for the North Atlantic Oscillation Index, here defined as the difference between daily sea level air pressure over Gibraltar and Iceland, were extracted from the Climatic Research Unit, University of East Anglia website (http://www.cru.uea.ac.uk/cru/data/nao.htm) (Chapter 3, Section 3.2, Table 4.1).

As with local precipitation and temperature data, monthly mean circulation indices were calculated as the mean daily value for the monthly precipitation collection period (i.e. between the 15th of successive months).

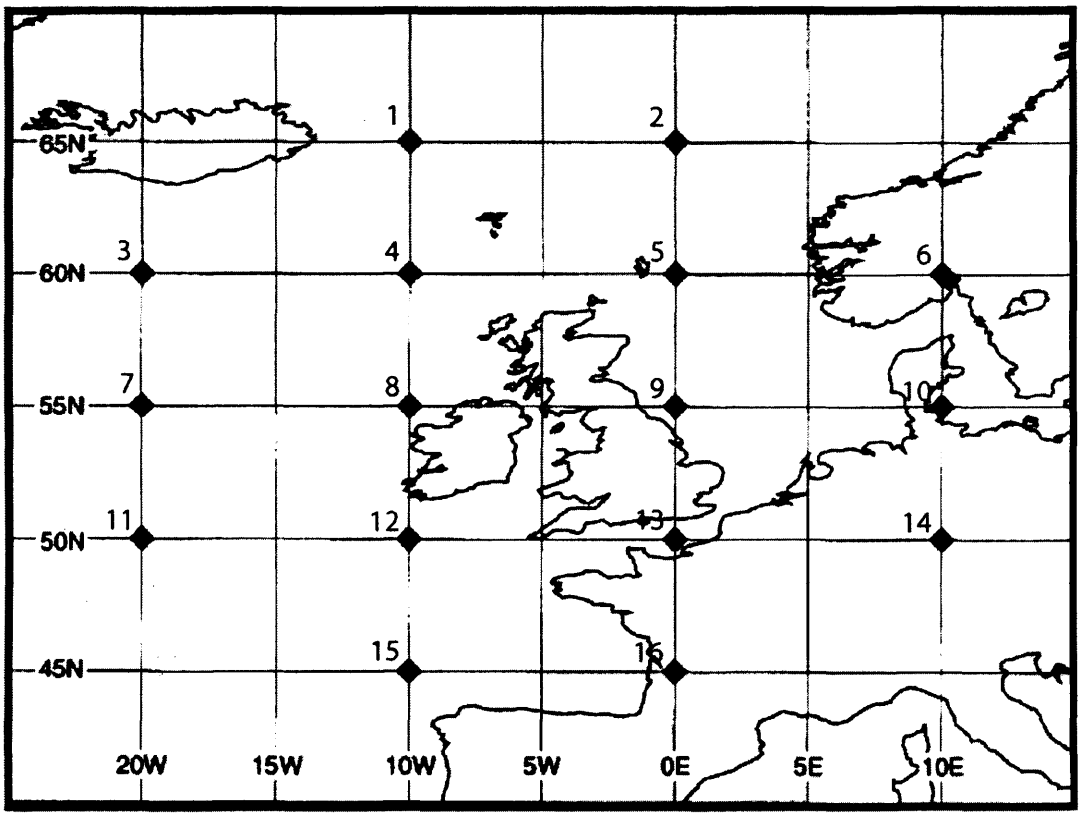

Figure 4.3 Grid points used for calculation of circulation indices (modified from Kilsby et al 1998)

4.2.2 Data analysis

The relationships between $\delta^{18}O_P$ and potential forcing agents were explored individually using correlation-probability matrices. Principal components analysis (PCA) was used to explore the covariance between the explanatory variables for each site, with units centered and standardised. Combinations of variables which together best explain $\delta^{18}O_P$ changes were assessed using multiple linear

regression. Model explanatory variables were selected based on prior theoretical knowledge and using three automated model fitting approaches: forwards and backwards stepwise regression (Venables and Ripley 2002) and best subsets regression (Miller 2002), using the Bayesian Information Criterion (BIC) as the measure for parameter inclusion/exclusion. Under the assumption that the model errors are normal, the BIC is calculated as:

$$BIC = n \ln\left(\frac{\mathrm{RSS}}{n}\right) + k \ln(n) \qquad (1)$$

where n is the number of observations, k is the number of free parameters to be estimated (i.e. the number of regressors, including the constant) and RSS is the residual sum of squares from the estimated model. BIC is an increasing function of RSS and k, and for any two models, that with the lower BIC is to be preferred.

For cases where the BIC statistic differed very little between models, ANOVA was used to test the significance of additional model components. Annual running means were calculated as the mean of the 12 preceding values in a time-series. Annual time-series were calculated for Wallingford and Valentia by taking the mean of monthly values of each parameter for each calendar year monitored.

4.3 Results

4.3.1 Regional airflow indices

Monthly mean air flow indices for the British Isles show contrasting patterns over the 23 years for which isotope monitoring data are available (Figures 4.4 and 4.5). None of the indices appear to demonstrate any significant long-term trend towards increasing or decreasing values since 1982, however inter-annual variability can be observed in some indices – in particular in westerly vorticity (*ZW*), North Atlantic Oscillation index (NAO) and in the directional frequency indices – most notably in the balance between north-westerly (*NW*) and southerly (*S*) air flows, whereby southerly flows are particularly frequent between 1994-1995 and in 2003, corresponding with fewer north-westerlies (Figure 4.4). Easterly and northerly air flows (*E*, *SE*, *NE*, *N*) are infrequent, characterised by occasional periods of high activity (Figure 4.4). Total wind velocity (*F*) is the most seasonally cyclical signal, whereas other variables – such as vorticity (*Z*, *ZW* and *ZS*) follows a more stochastic pattern, with notable peaks representing cyclonic activity, especially during 2000 (Figure 4.5).

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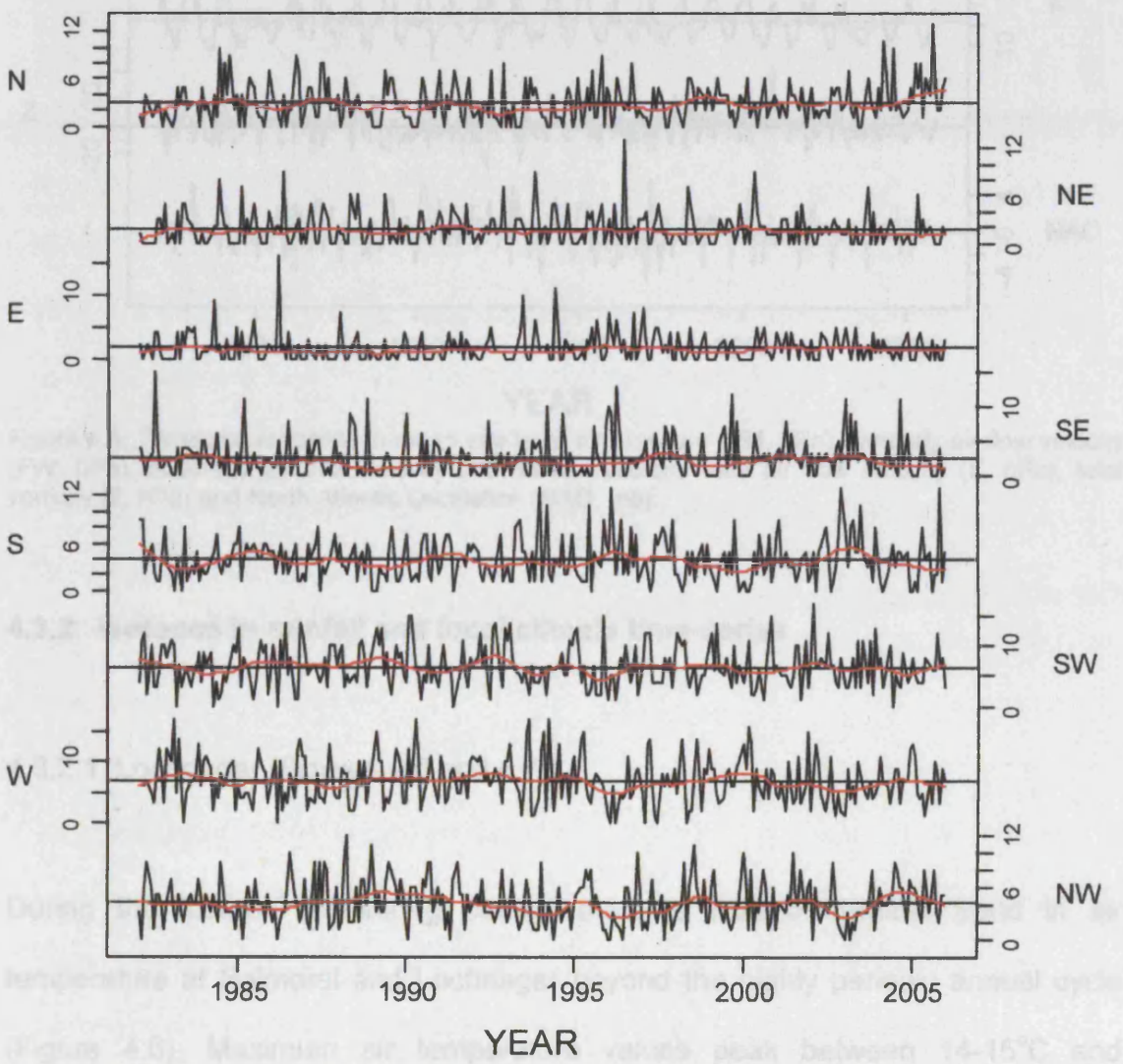

Figure 4.4: Temporal variability in frequency of directional air flow types (frequency of occurrences per month). N = northerly, NE = north-easterly, E = easterly, SE = south-easterly, S = southerly, SW = south-westerly, W = westerly and NW = north-westerly. See Table 1 for exact definition of directional types.

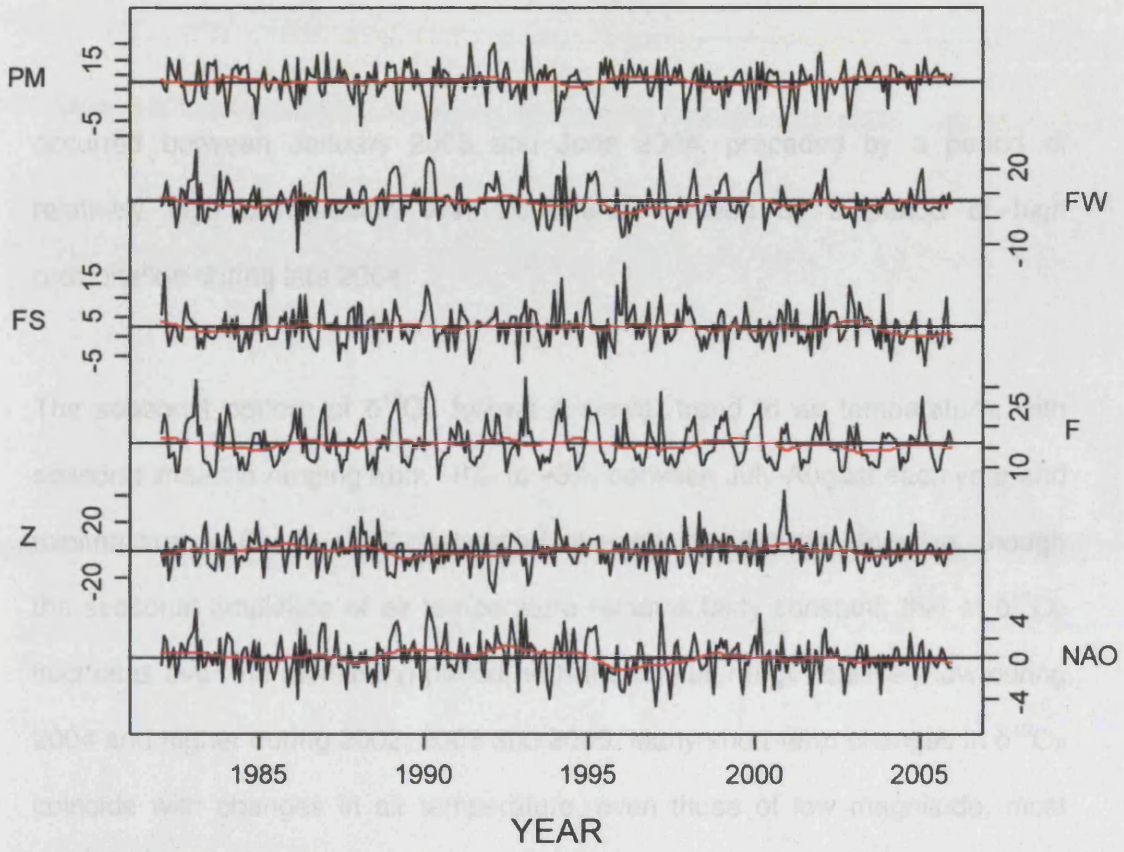

Figure 4.5. Temporal variability in mean sea level air pressure (PM, hPa), westerly air flow velocity (FW, hPa), southerly air flow velocity (FS, hPa), resultant total air flow velocity (F, hPa), total vorticity (Z, hPa) and North Atlantic Oscillation (NAO, mb).

4.3.2 Isotopes in rainfall and local climate time-series

4.3.2.1 Lochnagar (Figures 4.6 and 4.7)

During the isotope monitoring period, there is little discernible trend in air temperature at Balmoral and Lochnagar beyond the highly periodic annual cycle (Figure 4.6). Maximum air temperature values peak between 14-15°C and minimum values occur between 0-2°C. Precipitation amount varies markedly, however, with little seasonal cyclicity. A marked period of low precipitation

occurred between January 2003 and June 2004, preceded by a period of relatively high precipitation over 2002 and followed by a period of high precipitation during late 2004.

The seasonal pattern of $\delta^{18}O_P$ follows a similar trend to air temperature, with seasonal maxima ranging from –6‰ to –8‰ between July-August each year and minima from –10‰ to –12‰ between November and March. However, though the seasonal amplitude of air temperature remains fairly constant, that of $\delta^{18}O_P$ fluctuates over the monitoring period, with the annual range relatively low during 2004 and higher during 2002, 2003 and 2005. Many short-term changes in $\delta^{18}O_P$ coincide with changes in air temperature, even those of low magnitude, most notably during late 2002, and late 2003/early 2004 (Figure 4.6). In some cases, changes in $\delta^{18}O_P$ coincide with peaks in precipitation, although not consistently throughout the record. In particular, during the relatively wet year of 2002, high summer precipitation does not appear to correspond with any changes in $\delta^{18}O_P$ (Figure 4.6).

The biplot of $\delta^{18}O/\delta^{2}H$ in total precipitation at Lochnagar (Figure 4.7) defines a local meteoric water line (LMWL) of gradient 7.8, similar to the Global Meteoric Water Line, which has a gradient of 8 (Craig 1961). Snow waters plot away from this line, particularly at high δ values, describing a gradient of 8.8 (Figure 4.7).

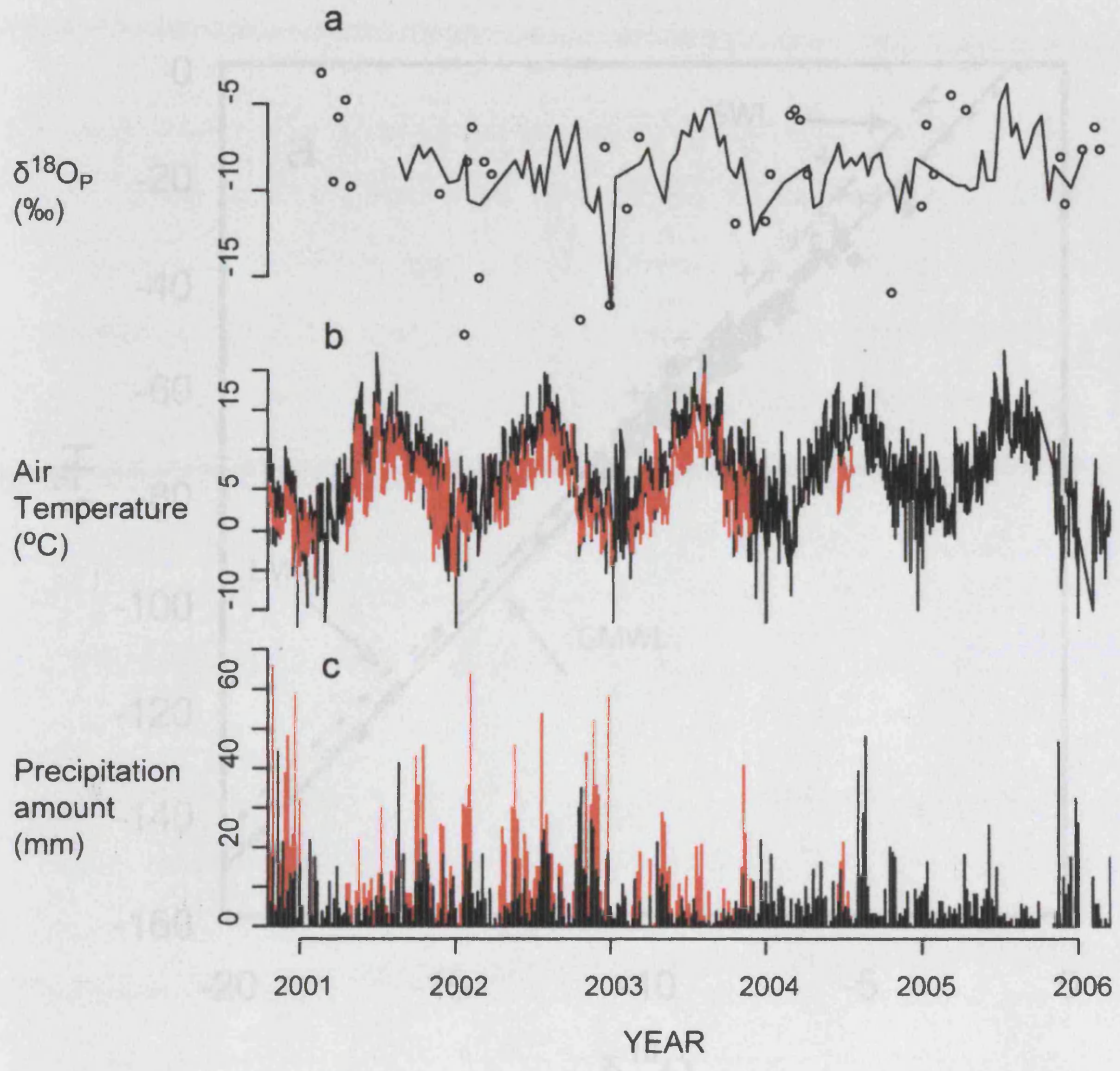

Figure 4.6. (a) $\delta^{18}O_P$ of total precipitation (solid line) and snow samples (points) at Lochnagar, 2001-2006; (b) Daily mean air temperature at Balmoral (black line) and Lochnagar (red line); (c) Daily precipitation amount at Balmoral (black line) and Lochnagar (red line).

4.3.2.2 Wallingford, Valentia and Keyworth (Figures 4.8-4.11)

The monthly datasets for isotopes in rainfall at Wallingford, Valentia and Keyworth, and their co-isotopic relationships are described in detail by Darling and Talbot (2003). None of the time series show definite long term trends but all

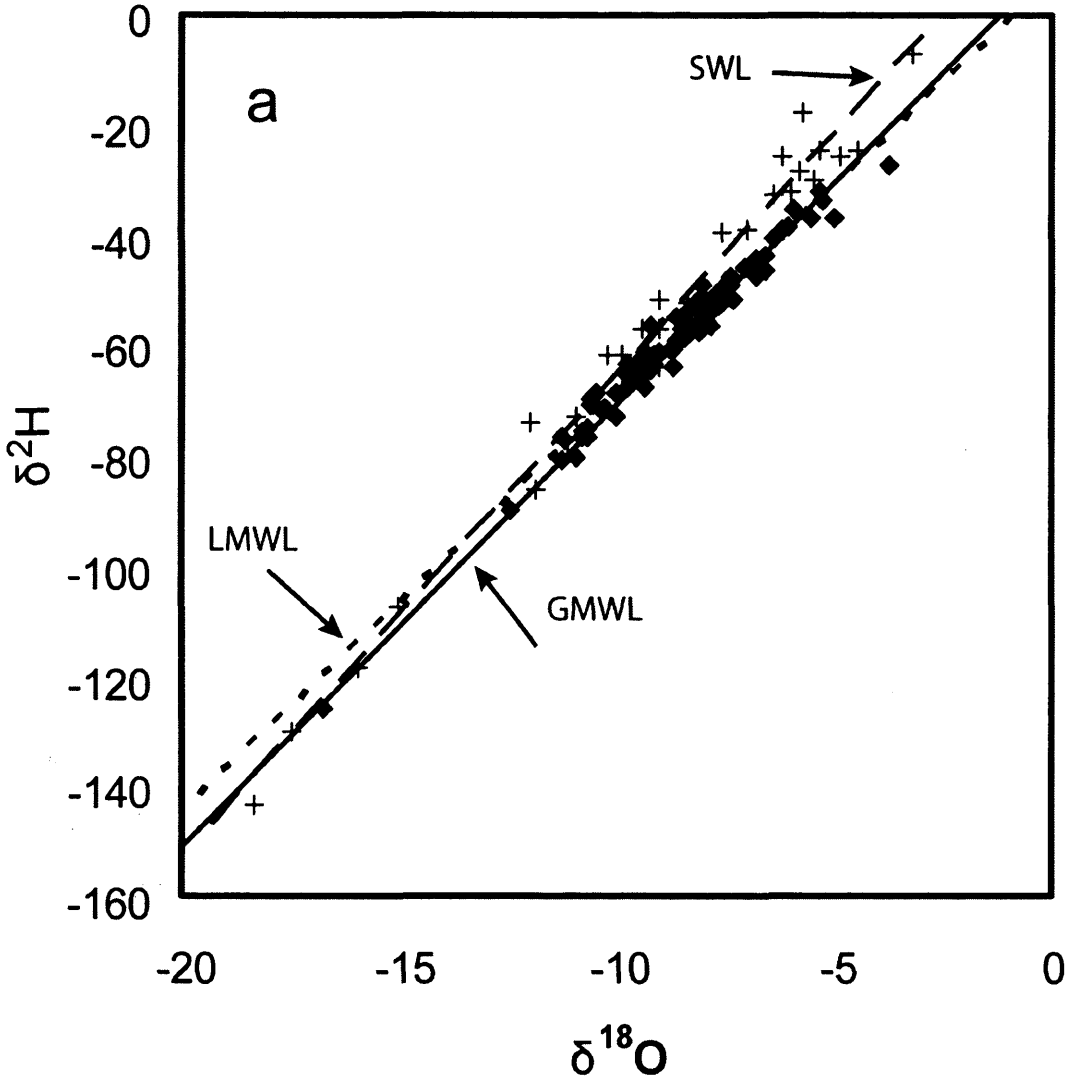

Figure 4.7: Bi plot of $\delta^{18}O$ vs δD for Lochnagar. Filled diamonds represent total precipitation values which define a local meteoric water line (LMWL; dotted line). Crosses represent isotope values measured from snow samples, defining a snow water line (SWL; dashed line). Solid line represents the global meteoric water line (GMWL).

display marked inter-annual variability, especially in the amplitude of seasonality between years. The standard deviations of Wallingford and Keyworth $\delta^{18}O_P$ are similar for the period of full overlap between the records (1985-1996) (2.20 and 2.31‰ respectively) (Figures 4.8 and 4.10) but Valentia is less (1.54‰) (Figure

4.9), reflecting the maritime climate at that site (Darling and Talbot 2003). In general, the isotope values from the three stations show similar patterns (Figure 4.11), apart from occasions when either of the English stations show an exaggerated version of the other station's response, or is out of step altogether (Darling and Talbot 2003). All three $\delta^{18}O_P$ time series show a moderate seasonal signal which corresponds with seasonal temperature patterns. Wallingford $\delta^{18}O_P$ also demonstrates a strong influence of precipitation amount, whereby periods of high precipitation, for example early 1990 and late 2005 correspond with low $\delta^{18}O_P$. This effect is less marked at Keyworth or Valentia, partially due to a lack of notable periods of distinctly high precipitation events in these datasets.

Time series of isotopes in rainfall from Lochnagar, Wallingford and Valentia overlap between 2001-2005 (Figure 4.12). Over the four years, Lochnagar $\delta^{18}O_P$ appears to correlate with values from both Valentia and Wallingford, although rarely both at the same time. In general, the three series show similar trends and seasonal patterns, however on a more detailed, monthly scale the relationship between the three is poor. $\delta^{18}O_P$ values from Lochnagar are consistently lower than those for Wallingford and Valentia, due to the higher altitude of that site. Lochnagar $\delta^{18}O_P$ values have a greater amplitude of variability and a more distinct seasonal pattern than those for Keyworth, Wallingford and Valentia, which demonstrate a greater degree of randomness in their monthly values and a weaker seasonal signal (Figure 4.12).

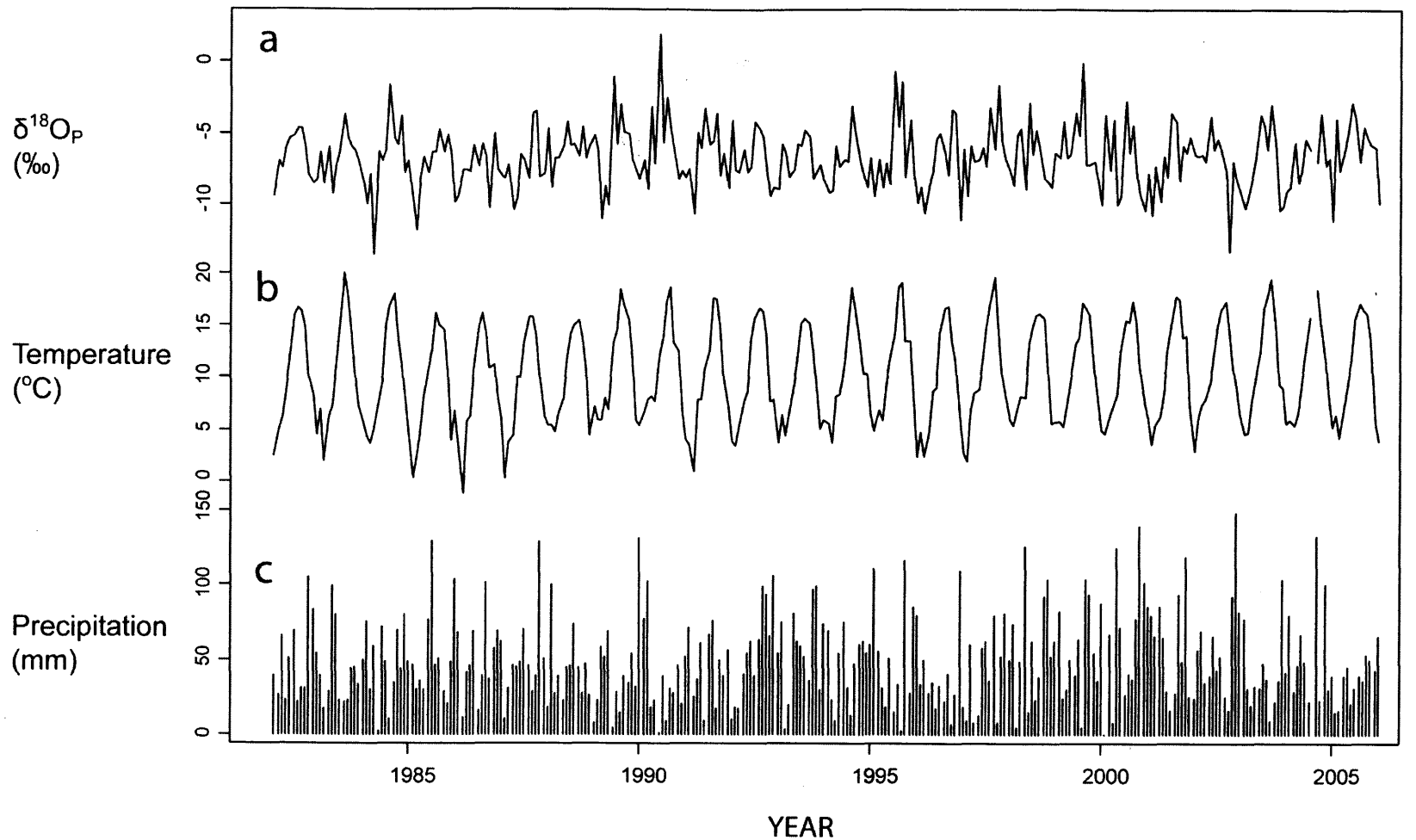

Figure 4.8: Wallingford time series of monthly oxygen isotopes in precipitation (a), monthly mean air temperature (b) and monthly precipitation amount (c). Data courtesy of IAEA (http://isohis.iaea.org).

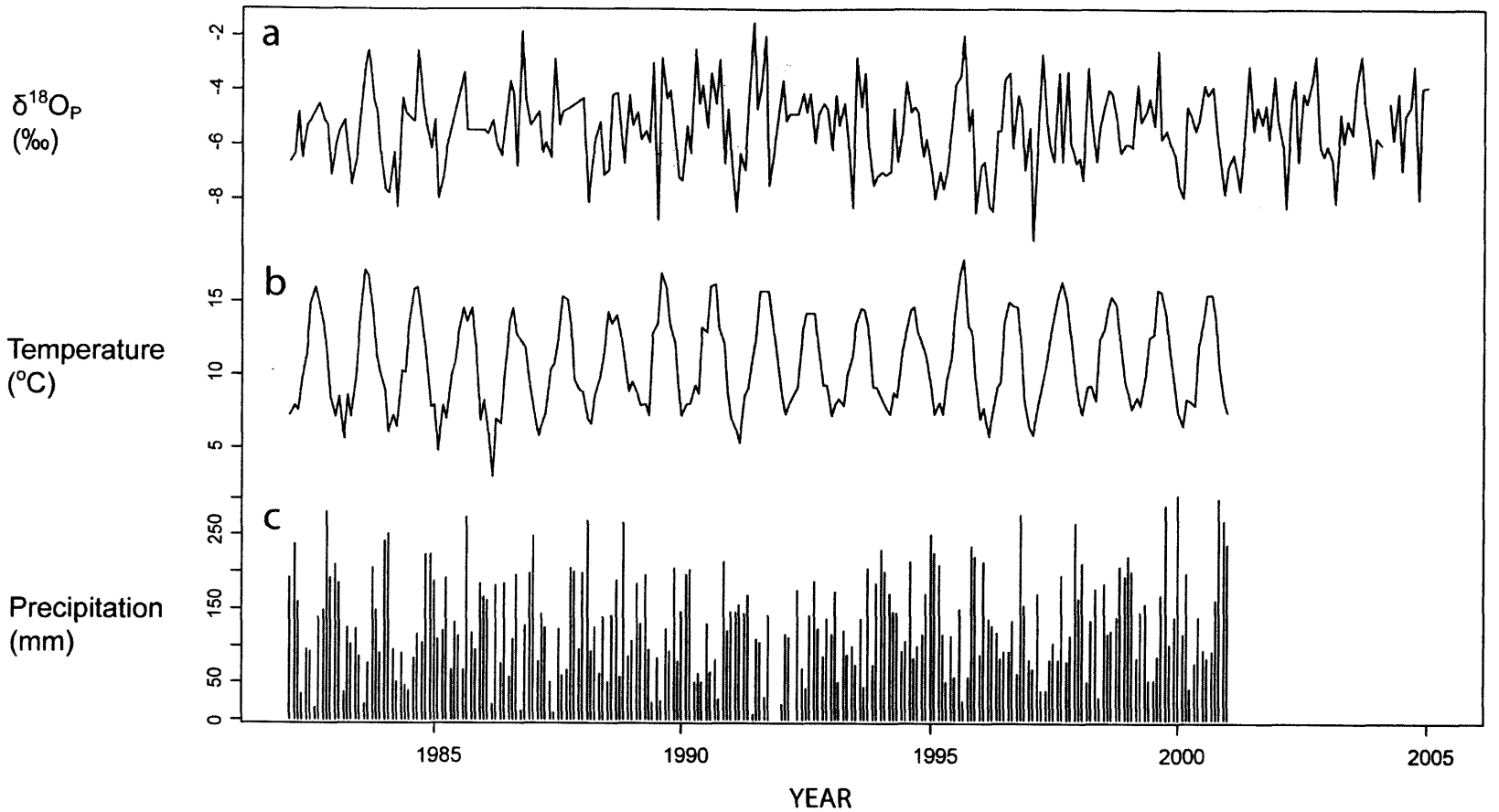

Figure 4.9: Valentia time series of monthly oxygen isotopes in precipitation (a), monthly mean air temperature (b) and monthly precipitation amount (c). Data courtesy of IAEA (http://isohis.iaea.org).

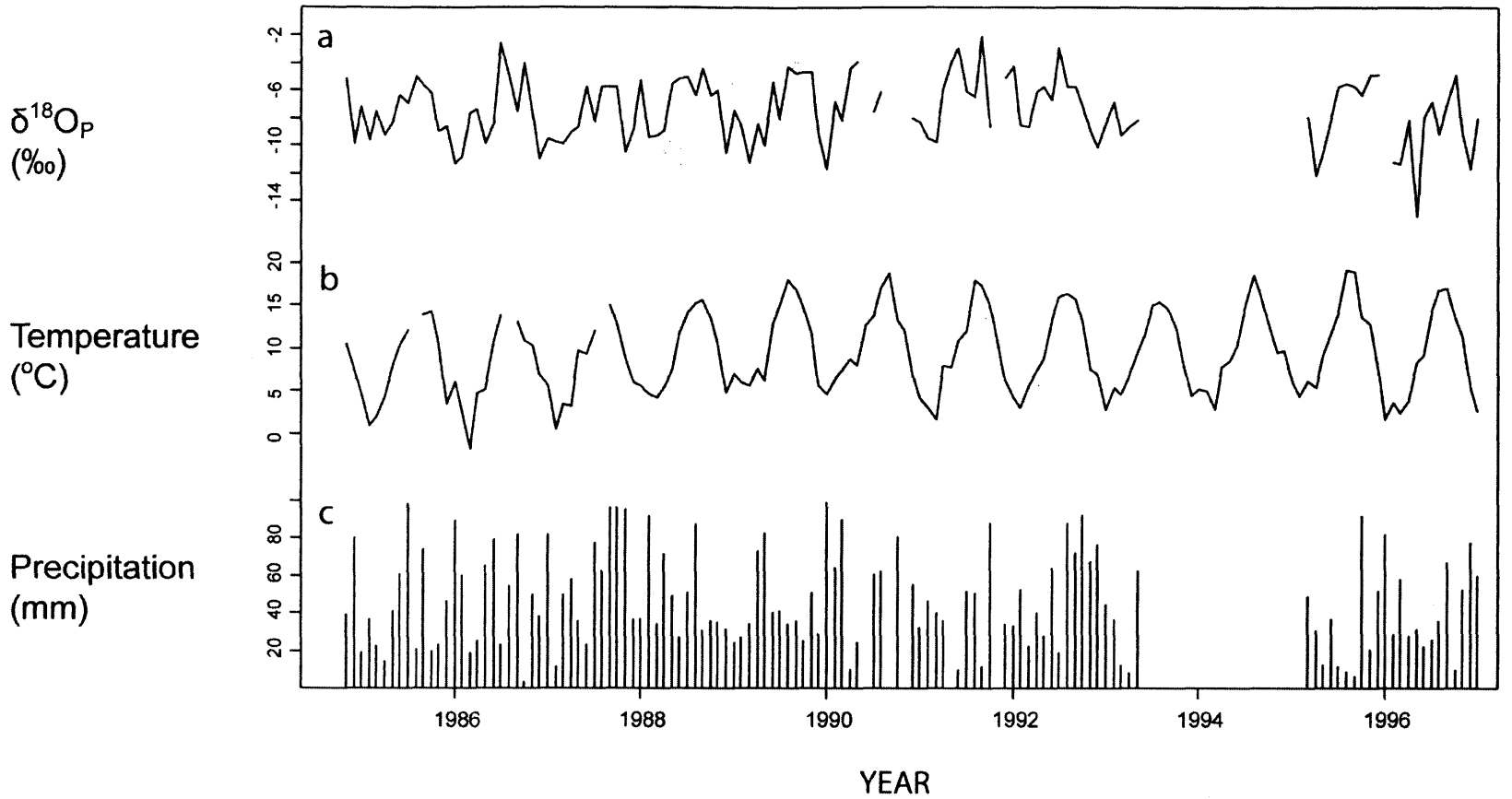

Figure 4.10: Keyworth time series of monthly oxygen isotopes in precipitation (a), monthly mean air temperature (b) and monthly precipitation amount (c). Data courtesy of IAEA (http://isohis.iaea.org).

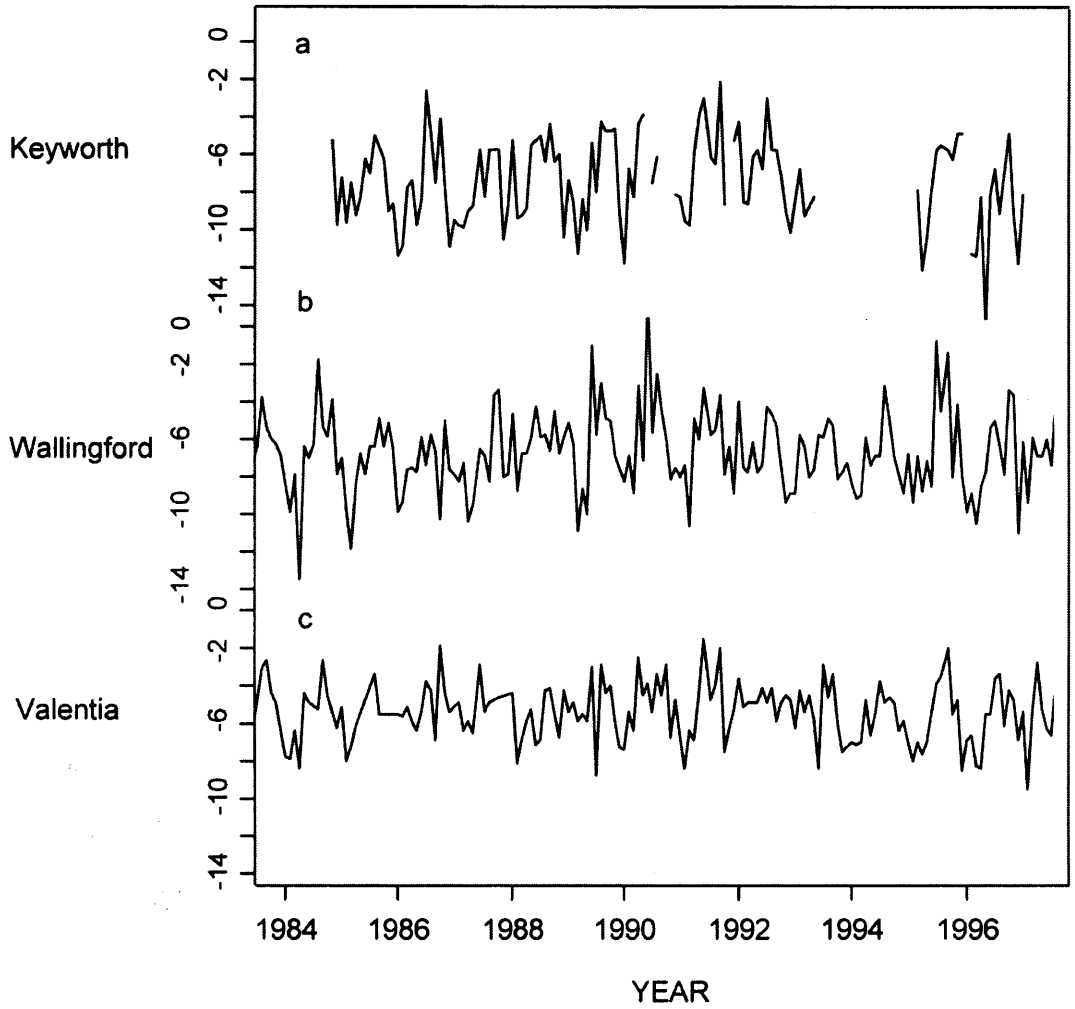

Figure 4.11: Comparison of monthly $\delta^{18}O_P$ for (a) Keyworth, (b) Wallingford and (c) Valentia, 1984 – 1997.

4.3.3 Exploratory data analysis

4.3.3.1 Principal components analysis (Figure 4.13)

In order to assess the predominant modes of weather, the regional and local climate indices were summarised for each site by means of principal components

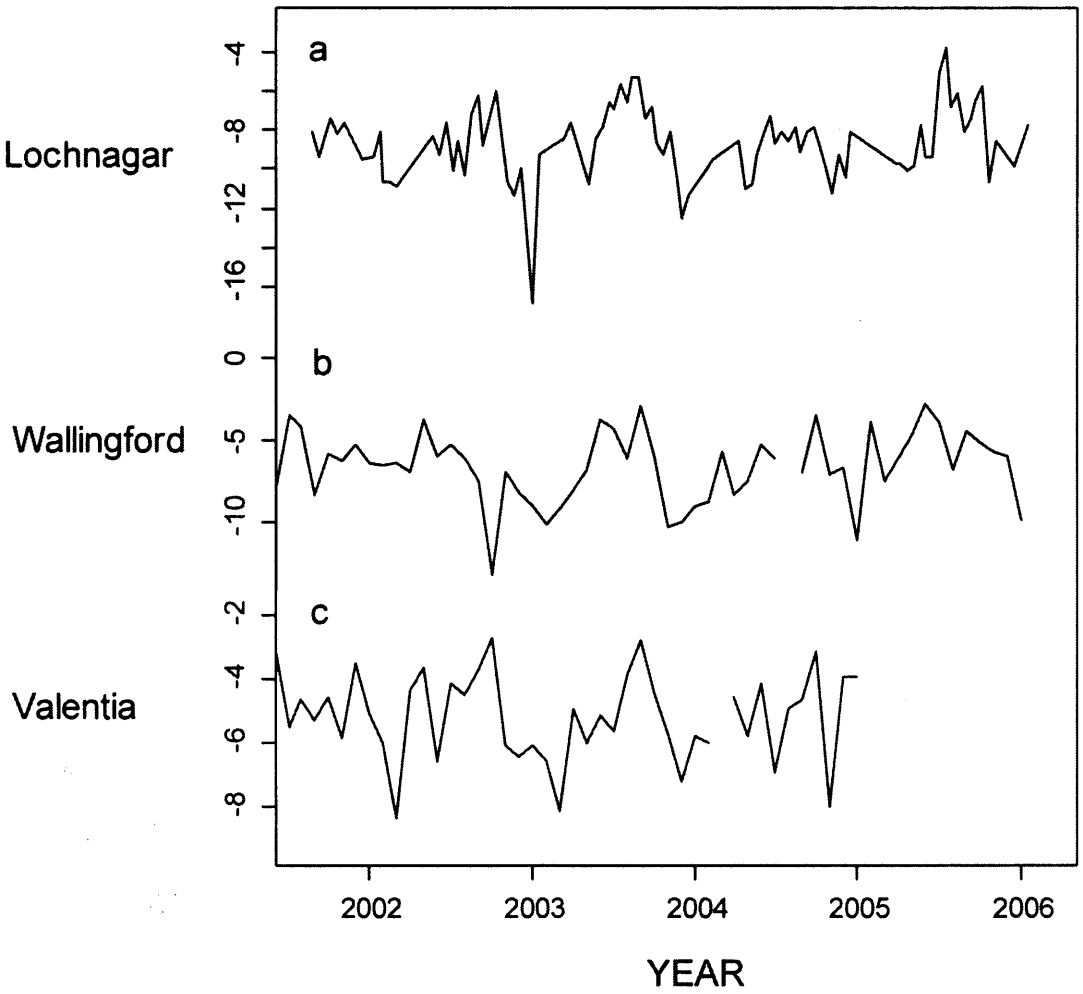

Figure 4.12: Comparison of $\delta^{18}O$ between Lochnagar, Wallingford and Valentia, 2001-2006. Solid lines represent monthly rain values.

analysis (PCA) (Figure 4.13). The PCA plots illustrate the degree of covariance between explanatory variables and are a useful means of summarising the climatic variability between sites. Although there are some minor differences, in general the association between local climate (temperature and precipitation amount) and the circulation indices is consistent between sites. Wallingford and Keyworth (Figure 4.13 a and c) demonstrate distinct groups of variables about

PCA axis 1, whereas at Valentia and Lochnagar (Figure 4.13 b and d) the vectors are more evenly distributed. At all sites, the first PCA axis is associated with meridional, NAO-type meteorological variability, characterised by a balance between high velocity south-westerly and westerly air flows coinciding with positive NAO, and northerly, north-easterly and easterly flows coinciding with negative NAO phases. The other notable pattern in all plots (i.e. PCA axis 2) is the balance between north-westerly circulation versus southerly flows (positive S and FS), whereby the latter are correlated with high precipitation amount and positive vorticity index (Z) indicating cyclonic weather. Temperature is poorly constrained by the first two PCA axes in all examples.

4.3.3.2 Correlation-probability matrices: Lochnagar (Table 4.2)

Correlation-probability matrices were derived for all explanatory variables and the response variable, $\delta^{18}O_P$ for each site (Tables 4.2-4.5). At Lochnagar, monthly average $\delta^{18}O_P$ is significantly correlated ($p<0.001$) with monthly air temperature at Balmoral ($R = 0.64$) and monthly mean wind flow velocity, *F* ($R = -0.53$), however *F* is also correlated with T. The correlation between precipitation amount, *P*, and $\delta^{18}O_P$ is inverse ($R = -0.24$) but not significant ($p = 0.15$).
Precipitation amount at Lochnagar is strongly correlated with air pressure (*PM*), vorticity (*Z*) and southerly wind force (*FS*), illustrating the relationship between cyclonic weather patterns and precipitation events, in particular when moist southerly air masses are involved.

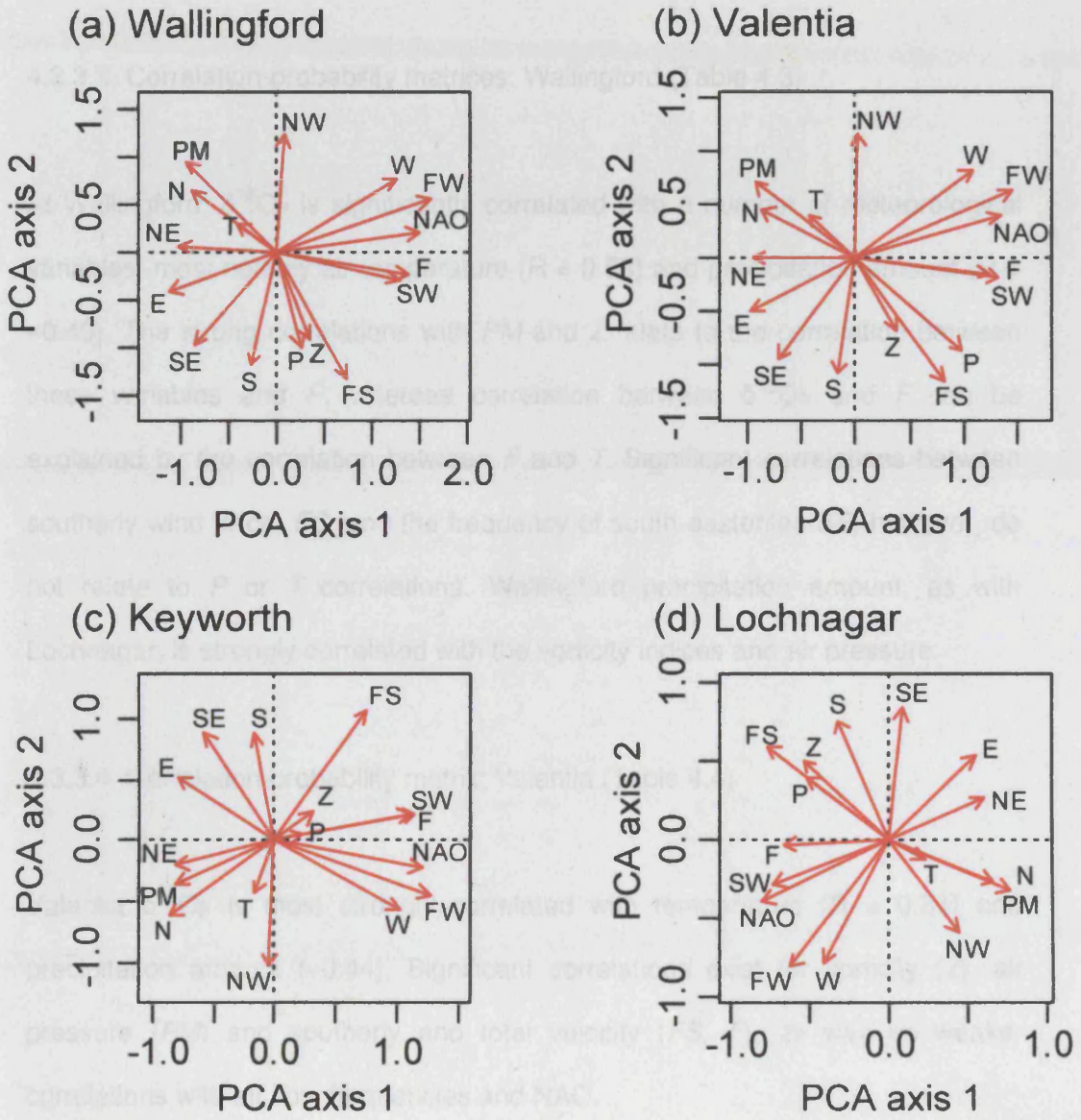

Figure 4.13: Principal components analysis of climate data for all four sites. T = air temperature (°C), P = precipitation amount (mm), PM = air pressure (hPa), FW = westerly air flow velocity (hPa), FS = southerly air flow velocity (hPa), F = resultant total air flow velocity (hPa), Z = total vorticity (hPa), NAO = North Atlantic Oscillation (mb). Wind flows (frequency of occurrences/month): N = northerly, NE = north-easterly, E = easterly, SE = south-easterly, S = southerly, SW = south-westerly, W = westerly and NW = north-westerly. See Table 1 for exact definition of directional types. Variance explained for axes 1 (A1) and 2 (A2) are as follows: Wallingford, A1 = 0.32, A2 = 0.20; Valentia, A1 = 0.35, A2 = 0.20; Keyworth, A1 = 0.34, A2 = 0.18; Lochnagar, A1 = 0.29, A2 = 0.24.

4.3.3.3 Correlation-probability matrices: Wallingford (Table 4.3)

At Wallingford, $\delta^{18}O_P$ is significantly correlated with a number of meteorological variables, most notably air temperature (R = 0.53) and precipitation amount (R = –0.46). The strong correlations with *PM* and *Z* relate to the correlation between these variables and *P*, whereas correlation between $\delta^{18}O_P$ and *F* can be explained by the correlation between *F* and *T*. Significant correlations between southerly wind force, *FS*, and the frequency of south easterlies *SE*, however, do not relate to *P* or *T* correlations. Wallingford precipitation amount, as with Lochnagar, is strongly correlated with the vorticity indices and air pressure.

4.3.3.4 Correlation-probability matrix: Valentia (Table 4.4)

Valentia $\delta^{18}O_P$ is most strongly correlated with temperature (R = 0.54) and precipitation amount (–0.44). Significant correlations exist for vorticity (*Z*), air pressure (*PM*) and southerly and total velocity (*FS, F*), as well as weaker correlations with air flow frequencies and NAO.

Table 4.2: Lochnagar correlation probability matrix. Values are the pearson product moment (*r*) with significant correlations (*p < 0.05)* highlighted in **bold type**.

	PM	FW	FS	F	Z	N	NE	E	SE	S	SW	W	NW	NAO	T	P
FW	-0.17															
FS	**-0.51**	-0.09														
F	**-0.48**	**0.60**	0.24													
Z	**-0.87**	-0.14	0.44	0.20												
N	0.35	-0.16	**-0.65**	-0.21	-0.25											
NE	0.12	-0.40	-0.34	-0.23	-0.04	0.23										
E	0.14	**-0.54**	-0.07	-0.04	-0.01	0.22	0.29									
SE	-0.09	**-0.62**	0.35	-0.09	0.23	-0.26	0.07	0.34								
S	-0.30	**-0.41**	**0.71**	0.01	0.31	**-0.41**	-0.09	0.10	0.39							
SW	-0.24	**0.43**	**0.54**	0.20	0.14	**-0.45**	**-0.43**	**-0.42**	-0.33	0.01						
W	-0.01	**0.77**	-0.25	0.24	-0.21	-0.13	-0.33	**-0.58**	**-0.48**	**-0.43**	0.12					
NW	0.26	0.19	**-0.70**	-0.22	-0.18	0.22	0.13	-0.12	-0.39	**-0.58**	-0.23	0.18				
NAO	-0.29	**0.61**	0.37	0.31	0.11	-0.35	**-0.51**	**-0.61**	-0.27	0.05	**0.60**	**0.44**	-0.19			
T	0.05	-0.24	-0.07	**-0.74**	0.09	-0.09	0.14	-0.21	-0.09	-0.03	0.08	-0.02	0.27	0.01		
P	**-0.64**	-0.03	0.31	0.28	**0.70**	-0.18	-0.08	-0.13	0.28	0.16	0.06	-0.01	-0.17	0.02	-0.17	
$\delta^{18}O$	0.24	-0.19	-0.03	**-0.53**	-0.14	-0.01	0.08	-0.09	-0.05	-0.07	0.11	-0.07	0.13	0.00	**0.64**	-0.24

Table 4.3: Correlation probability matrix, Wallingford. Values are the pearson product moment (*r*) with significant correlations ($p < 0.05$) highlighted in **bold type**.

	PM	FW	FS	F	Z	N	NE	E	SE	S	SW	W	NW	NAO	T	P
FW	**-0.32**															
FS	**-0.38**	0.13														
F	**-0.51**	**0.75**	**0.41**													
Z	**-0.83**	0.00	0.13	**0.17**												
N	**0.24**	**-0.31**	**-0.63**	**-0.36**	-0.01											
NE	**0.17**	**-0.49**	**-0.41**	**-0.37**	0.03	**0.33**										
E	**0.23**	**-0.62**	-0.08	**-0.30**	-0.12	0.08	**0.32**									
SE	0.08	**-0.61**	**0.27**	**-0.27**	0.01	-0.11	0.04	**0.37**								
S	-0.11	**-0.37**	**0.57**	-0.12	0.16	**-0.22**	-0.13	0.06	**0.33**							
SW	**-0.36**	**0.59**	**0.54**	**0.46**	0.12	**-0.48**	**-0.41**	**-0.42**	**-0.37**	-0.07						
W	-0.14	**0.80**	-0.05	**0.47**	-0.11	**-0.29**	**-0.40**	**-0.52**	**-0.52**	**-0.43**	**0.29**					
NW	0.17	**0.26**	**-0.61**	-0.08	-0.08	**0.19**	-0.12	**-0.27**	**-0.40**	**-0.42**	-0.16	0.19				
NAO	**-0.30**	**0.79**	**0.30**	**0.57**	0.05	**-0.42**	**-0.49**	**-0.57**	**-0.44**	-0.14	**0.60**	**0.66**	0.08			
T	0.17	**-0.21**	**-0.19**	**-0.61**	0.00	0.06	-0.02	-0.05	0.02	0.02	-0.06	-0.03	0.17	-0.07		
P	**-0.66**	-0.04	**0.21**	0.14	**0.68**	-0.03	0.06	-0.04	0.11	0.13	0.12	-0.10	**-0.23**	0.01	-0.04	
$\delta^{18}O$	**0.36**	0.03	-0.16	**-0.28**	**-0.30**	0.04	-0.07	-0.08	-0.12	-0.05	0.00	0.11	0.17	0.05	**0.53**	**-0.46**

Table 4.4 Valentia correlation probability matrix. Values are the pearson product moment (*r*) with significant correlations (*p < 0.05)* highlighted in **bold type**.

	PM	FW	FS	F	Z	N	NE	E	SE	S	SW	W	NW	NAO	T	P
FW	**-0.34**															
FS	**-0.36**	0.18														
F	**-0.51**	**0.76**	**0.48**													
Z	**-0.82**	0.00	0.08	0.15												
N	**0.21**	**-0.37**	**-0.62**	**-0.44**	0.06											
NE	0.17	**-0.51**	**-0.43**	**-0.40**	0.05	**0.40**										
E	**0.25**	**-0.63**	-0.09	**-0.31**	-0.13	0.07	**0.31**									
SE	0.11	**-0.62**	**0.24**	**-0.28**	-0.01	-0.07	0.04	**0.37**								
S	-0.07	**-0.37**	**0.52**	-0.13	0.14	-0.18	-0.12	0.06	**0.31**							
SW	**-0.40**	**0.64**	**0.55**	**0.54**	0.13	**-0.48**	**-0.41**	**-0.44**	**-0.39**	-0.11						
W	-0.15	**0.81**	-0.01	**0.49**	-0.12	**-0.33**	**-0.42**	**-0.51**	**-0.53**	**-0.43**	**0.32**					
NW	0.18	**0.26**	**-0.58**	-0.09	-0.09	0.17	-0.17	**-0.29**	**-0.40**	**-0.38**	-0.13	0.19				
NAO	**-0.29**	**0.82**	**0.29**	**0.59**	0.04	**-0.43**	**-0.49**	**-0.59**	**-0.48**	-0.16	**0.61**	**0.68**	0.13			
T	**0.26**	**-0.20**	**-0.23**	**-0.59**	-0.10	0.11	-0.08	-0.05	0.04	0.04	-0.14	0.01	0.18	-0.09		
P	**-0.74**	**0.33**	**0.56**	**0.52**	**0.57**	**-0.28**	**-0.31**	**-0.29**	-0.03	**0.23**	**0.47**	0.13	**-0.25**	**0.29**	**-0.22**	
$\delta^{18}O$	**0.40**	0.10	**-0.23**	**-0.25**	**-0.38**	0.00	-0.08	-0.12	**-0.21**	-0.15	-0.01	**0.26**	**0.21**	0.16	**0.54**	**-0.44**

Table 4.5: Keyworth correlation probability matrix. Values are the pearson product moment (*r*) with significant correlations ($p < 0.05$) highlighted in **bold type**.

	PM	FW	FS	F	Z	N	NE	E	SE	S	SW	W	NW	NAO	T	P
FW	**-0.41**															
FS	**-0.37**	0.25														
F	**-0.51**	**0.76**	**0.52**													
Z	**-0.80**	0.05	0.08	0.14												
N	**0.29**	**-0.42**	**-0.69**	-0.51	0.03											
NE	0.19	**-0.49**	**-0.48**	**-0.45**	0.02	**0.42**										
E	**0.27**	-0.62	-0.06	-0.25	-0.21	0.03	**0.28**									
SE	0.14	**-0.58**	**0.26**	-0.20	-0.05	-0.06	-0.04	**0.35**								
S	-0.05	**-0.33**	**0.45**	-0.15	0.17	-0.16	-0.17	0.04	**0.30**							
SW	**-0.44**	**0.67**	**0.63**	**0.56**	0.12	**-0.60**	**-0.44**	**-0.43**	**-0.33**	-0.09						
W	-0.20	**0.82**	0.08	**0.51**	-0.08	**-0.38**	**-0.41**	**-0.47**	**-0.55**	**-0.40**	**0.45**					
NW	0.15	0.20	**-0.61**	-0.09	-0.02	**0.26**	-0.10	**-0.31**	**-0.33**	**-0.32**	-0.25	0.10				
NAO	**-0.40**	**0.83**	**0.35**	**0.60**	0.14	**-0.49**	**-0.49**	**-0.56**	**-0.44**	-0.16	**0.70**	**0.67**	0.06			
T	0.14	-0.09	-0.20	**-0.51**	0.02	0.13	-0.06	-0.14	-0.11	0.01	-0.03	0.07	0.20	0.05		
P	**-0.51**	0.07	0.03	0.01	**0.56**	0.07	0.06	-0.22	-0.06	0.02	0.12	0.00	-0.02	0.07	0.06	
$\delta^{18}O$	**0.30**	-0.06	-0.17	**-0.29**	-0.26	0.07	-0.03	0.10	-0.01	-0.16	-0.07	0.08	0.09	0.00	**0.57**	-0.24

4.3.3.5 Correlation-probability matrix: Keyworth (Table 4.5)

The strongest correlation with Keyworth $\delta^{18}O_P$ is with air temperature (R = 0.57) with a weaker, yet significant correlation with precipitation amount (R = -0.24). Correlations also exist with air pressure, wind velocity and vorticity.

4.3.4 Multiple regression

In order to identify a set of climatic variables which best explain $\delta^{18}O_P$ for each site, three automatic selection procedures (backward stepwise regression: BSTEP; forwards stepwise regression: FSTEP and best subsets regression: BSUB) were used, using the Bayesian Information Criterion (BIC) as a means of critically evaluating the value of a model parameter (Miller 2002; Venables and Ripley 2002). In order to avoid problems associated with multicollinearity between predictors, the variance inflation factor statistic (VIF) was monitored: where VIF <2 it was assumed that there was no significant correlation between predictors (Jongman *et al.* 1987; Leps and Smilauer 2000). By using three different selection criteria, in addition to prior theoretical knowledge of potential controls over $\delta^{18}O_P$, the most parsimonious model was identified for each site.

4.3.4.1 Wallingford multiple regression

Figure 4.14a illustrates the relationship between model size (number of components) and effectiveness according to BIC for the five best model subsets as calculated by best subsets regression of the Wallingford dataset. The optimal model size for Wallingford is three components, with subsequent component inclusion leading to a decline in model efficiency (indicated by an increase in BIC). All three selection criteria (BSTEP, FSTEP and BSUB) select the same predictor variables: air temperature (*T*), precipitation amount (*P*) and the force of westerly flow (*FW*) (Table 4.6). The combined R^2 for this three component model is 0.49, with $p < 0.001$. The plot of observed vs. predicted values (Figure 4.14b) demonstrates a reasonable fit, however there are at least two notable outliers and a good deal of variability remains unexplained. There is also a degree of model conservatism, with the model under-predicting high δ values and over-predicting low δ values. This is evident by comparing the time-series of modelled with observed $\delta^{18}O_P$ values (Figure 4.14c) – in general, the model explains much of the short term variability, however extreme summer (e.g. 1990) and winter (e.g. 1984 and 2003) values are poorly reproduced. 12 month running mean values for modelled and observed monthly values are very close in general, again except for years which experienced marked positive or negative $\delta^{18}O_P$ values, such as 1984, 1990, 1999 and 2003.

Table 4.6: Wallingford multiple regression models according to different selection criteria. BStep refers to backwards stepwise selection (Venables and Ripley 2002), FStep refers to forwards stepwise selection (Venables and Ripley 2002), best subsets refers to best subsets regression (Miller 2002). c = number of model components; T = monthly mean daily air temperature (K); P = monthly mean daily precipitation amount (mm), FW = monthly mean daily westerly flow velocity (hPa).

SITE: Wallingford		
$N = 285$		
Method	**Model**	**R^2**
BStep	T+P+FW	0.4895
FStep	T+P+FW	0.4895
Best subsets (c=2)	T+P	0.4766
Best subsets (c=3)	T+P+FW	0.4895
FINAL MODEL	**$\delta^{18}O_P = 0.25T - 0.032P + 0.041FW - 76.27$**	

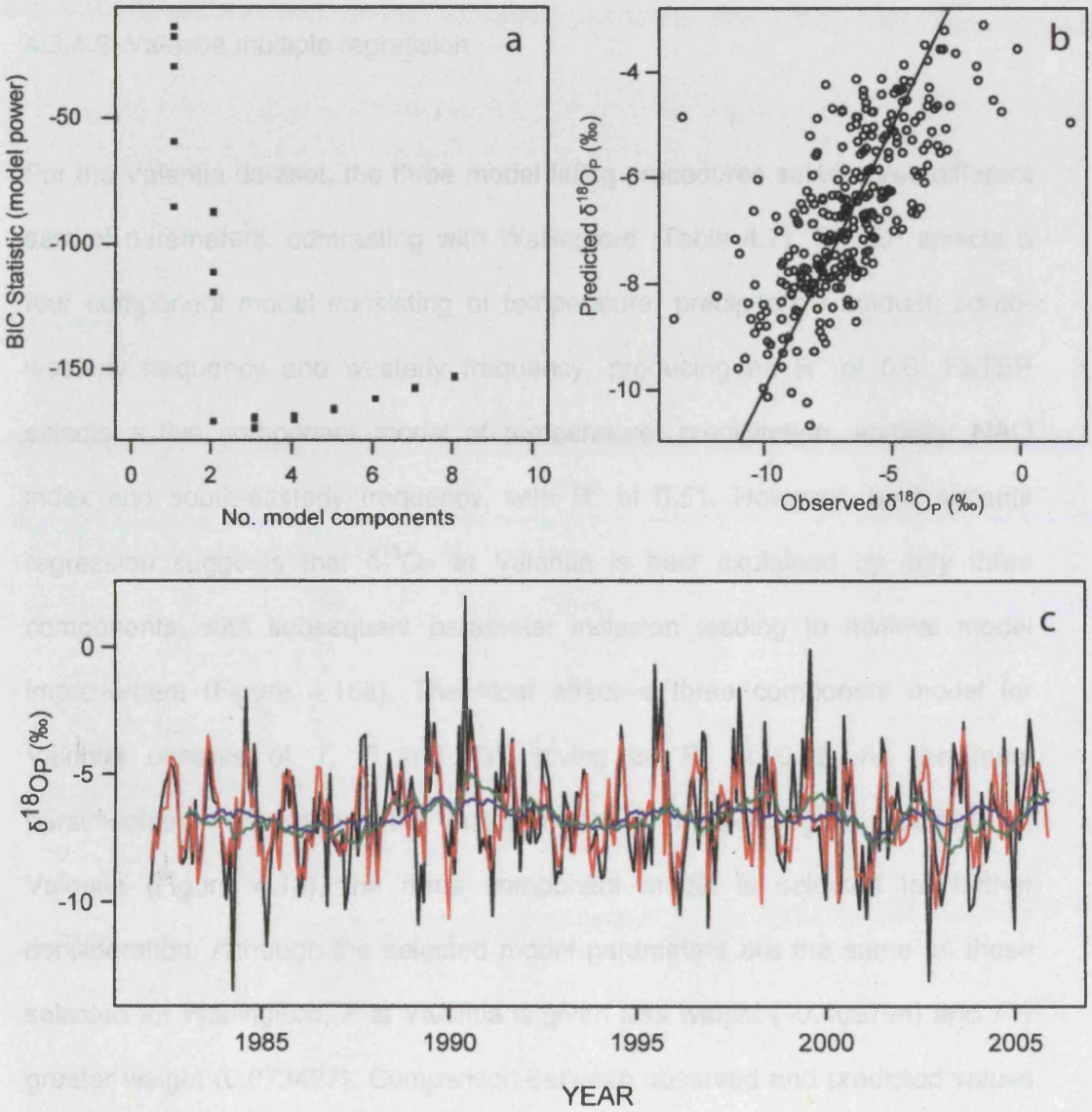

Figure 4.14: Multiple regression plots for Wallingford $\delta^{18}O_P$ data, using final model in Table 6. (a) Model power (Bayesian Information Criterion) vs. model size (number of components) for 5 best model subsets; (b) Observed vs. predicted $\delta^{18}O_P$; (c) Comparison of observed (black line) and predicted (red line) monthly $\delta^{18}O_P$. Green line = annual running mean of observed data and blue line = annual running mean for predicted values.

4.3.4.2 Valentia multiple regression

For the Valentia dataset, the three model fitting procedures select three different sets of parameters, contrasting with Wallingford (Table 4.7). BSTEP selects a four component model consisting of temperature, precipitation amount, south-westerly frequency and westerly frequency, producing an R^2 of 0.5. FSTEP selects a five component model of temperature, precipitation, vorticity, NAO index and south-easterly frequency, with R^2 of 0.51. However, best subsets regression suggests that $\delta^{18}O_P$ at Valentia is best explained by only three components, with subsequent parameter inclusion leading to minimal model improvement (Figure 4.15a). The most effective three component model for Valentia consists of *T*, *P* and *FW*, giving an R^2 of 0.49. As the most parsimonious, representing the major modes of meteorological variability at Valentia (Figure 4.13), the three component model is selected for further consideration. Although the selected model parameters are the same as those selected for Wallingford, *P* at Valentia is given less weight (–0.009794) and *FW* greater weight (0.073427). Comparison between observed and predicted values (Figure 4.15b) demonstrates a clear decrease in predictive capacity for low δ values and again there are a number of marked outliers. As for Wallingford, comparison of modelled and observed time series demonstrates an inability to effectively model extreme values, however periods of divergence between the two at Valentia are more frequent and in some cases more prolonged (e.g. over 1995) (Figure 4.15c). Despite this, the 12 month running means of predicted and

observed closely correspond, except for the divergence over 1995 (the divergence at ~1986 corresponds with a period of missing data) (Figure 4.15c).

Table 4.7: Valentia multiple regression models according to different selection criteria. BStep refers to backwards stepwise selection (Venables and Ripley 2002), FStep refers to forwards stepwise selection (Venables and Ripley 2002), best subsets refers to best subsets regression (Miller 2002). c = number of model components; T = monthly mean daily air temperature (K); P = monthly mean daily precipitation amount (mm), FW = monthly mean daily westerly flow velocity (hPa).

SITE: Valentia		
n = 208		
Method	**Model**	**R^2**
BStep	SW + W + T + P	0.5044
FStep	T + Z + SE + P + NAO	0.5122
Best subsets (c=3)	T+ P + FW	0.4943
FINAL MODEL	**$\delta^{18}O_P = 0.24T - 0.0098P + 0.074FW - 72.78$**	

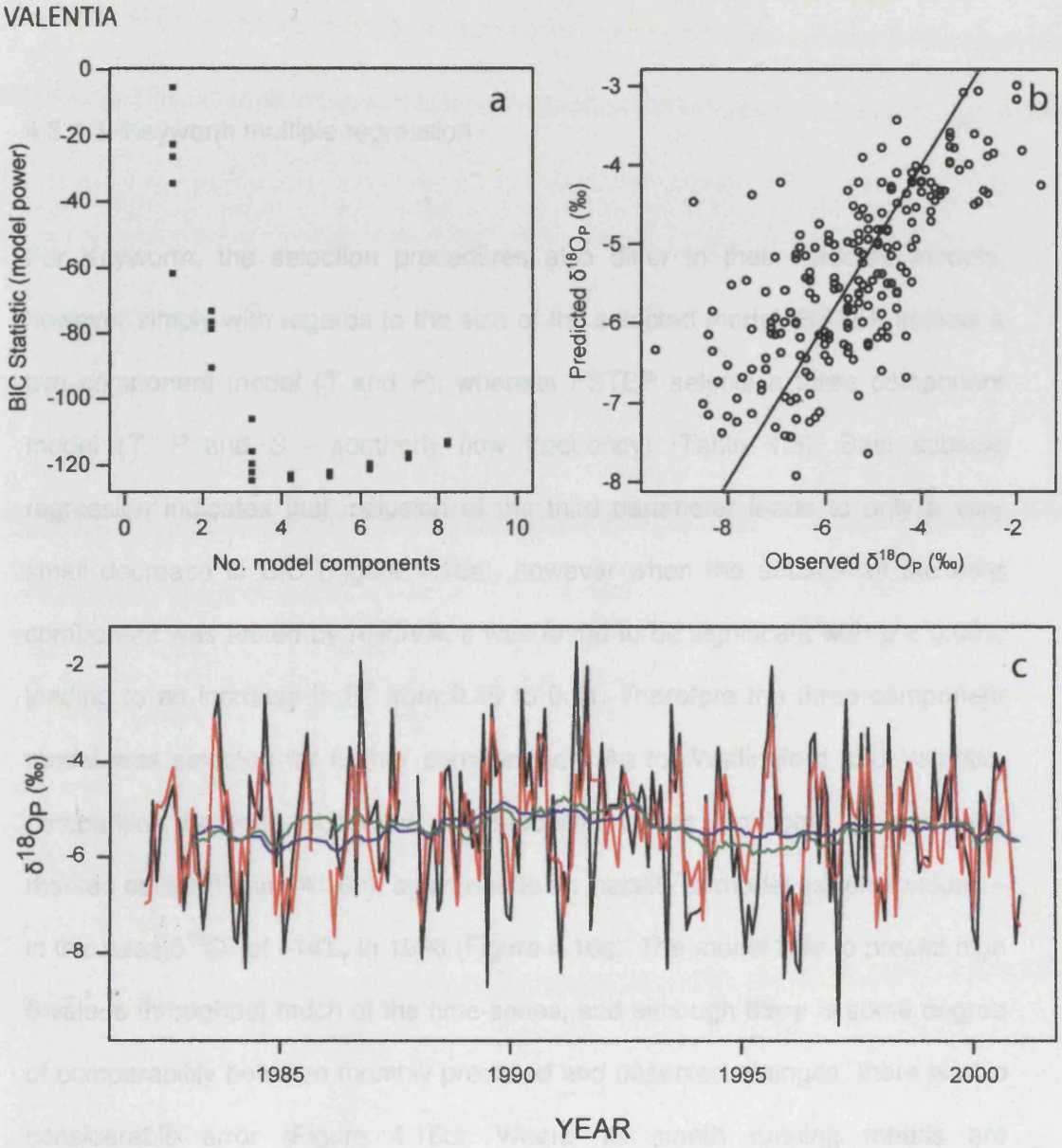

Figure 4.15: Multiple regression plots for Valentia $\delta^{18}O_P$ data, using final model in Table 7. (a) Model power (Bayesian Information Criterion) vs. model size (number of components) for 5 best model subsets; (b) Observed vs. predicted $\delta^{18}O_P$; (c) Comparison of observed (black line) and predicted (red line) monthly $\delta^{18}O_P$. Green line = annual running mean of observed data and blue line = annual running mean for predicted values.

4.3.4.3 Keyworth multiple regression

For Keyworth, the selection procedures also differ in their selected models, however simply with regards to the size of the selected model. BSTEP selects a two component model (*T* and *P*), whereas FSTEP selects a three component model (*T*, *P* and *S* - southerly flow frequency) (Table 4.8). Best subsets regression indicates that inclusion of the third parameter leads to only a very small decrease in BIC (Figure 4.16a), however when the addition of the third component was tested by ANOVA, it was found to be significant with $p < 0.001$, leading to an increase in R^2 from 0.39 to 0.41. Therefore the three component model was selected for further consideration. As for Wallingford and Valentia, comparison between observed and modelled values highlights at least one marked outlier (Figure 4.16b), again due to an inability to model extreme values – in this case $\delta^{18}O_P$ of –14‰ in 1996 (Figure 4.16c). The model fails to predict high δ values throughout much of the time-series, and although there is some degree of comparability between monthly predicted and observed changes, there is also considerable error (Figure 4.16c). Where 12 month running means are concerned, modelled $\delta^{18}O_P$ values fail to fully account for the increases in $\delta^{18}O_P$ between 1988-1993 and the subsequent decrease from 1994 onward (Figure 4.16c).

Table 4.8. Keyworth multiple regression models according to different selection criteria. BStep refers to backwards stepwise selection (Venables and Ripley 2002), FStep refers to forwards stepwise selection (Venables and Ripley 2002), best subsets refers to best subsets regression (Miller 2002). c = number of model components; *T* = monthly mean daily air temperature (K); *P* = monthly mean daily precipitation amount (mm), *FW* = monthly mean daily westerly flow velocity (hPa).

SITE: Keyworth		
$n = 114$		
Method	**Model**	**R^2**
BStep	T+P	0.39
FStep	T + P + S	0.4103
Best subsets (c=2)	T+P	0.39
Best subsets (c=3)	T+P+S	0.4103
FINAL MODEL	**$\delta^{18}O_P = 0.28T - 0.025P - 0.14S - 84.43$**	

KEYWORTH

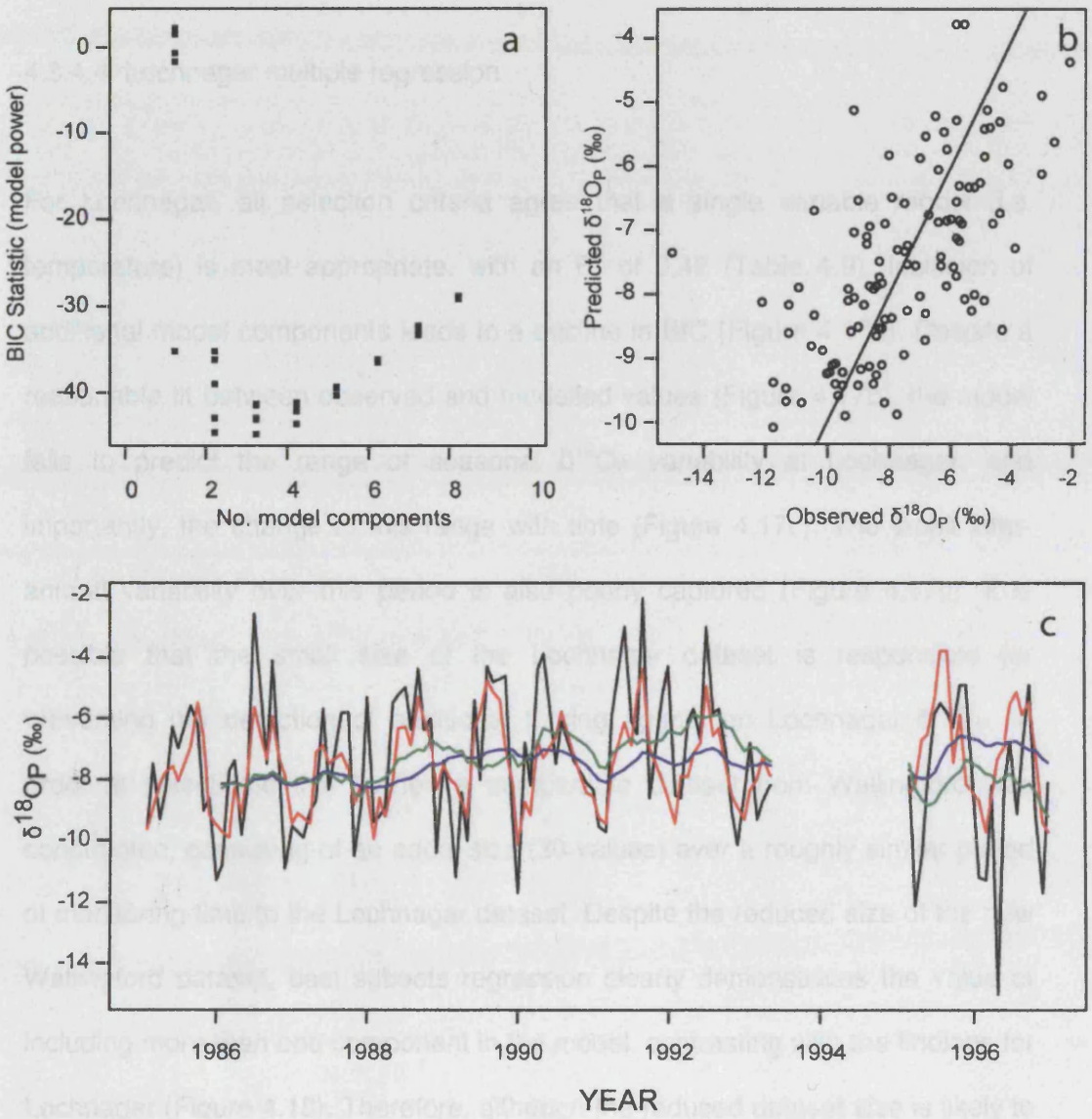

Figure 4.16: Multiple regression plots for Keyworth $\delta^{18}O_P$ data, using final model in Table 8. (a) Model power (Bayesian Information Criterion) vs. model size (number of components) for 5 best model subsets; (b) Observed vs. predicted $\delta^{18}O_P$; (c) Comparison of observed (black line) and predicted (red line) monthly $\delta^{18}O_P$. Green line = annual running mean of observed data and blue line = annual running mean for predicted values.

4.3.4.4 Lochnagar multiple regression

For Lochnagar, all selection criteria agree that a single variable model (i.e. temperature) is most appropriate, with an R^2 of 0.42 (Table 4.9). Inclusion of additional model components leads to a decline in BIC (Figure 4.17a). Despite a reasonable fit between observed and modelled values (Figure 4.17b), the model fails to predict the range of seasonal $\delta^{18}O_P$ variability at Lochnagar, and importantly, the change in this range with time (Figure 4.17c). The small inter-annual variability over this period is also poorly captured (Figure 4.17c). It is possible that the small size of the Lochnagar dataset is responsible for preventing the detection of additional forcing agents on Lochnagar $\delta^{18}O_P$. In order to investigate this further, a comparable dataset from Wallingford was constructed, consisting of an equal size (30 values) over a roughly similar period of monitoring time to the Lochnagar dataset. Despite the reduced size of the new Wallingford dataset, best subsets regression clearly demonstrates the value of including more than one component in the model, contrasting with the findings for Lochnagar (Figure 4.18). Therefore, although the reduced dataset size is likely to have some effect on the number of model components which explain $\delta^{18}O_P$ at Lochnagar, it is also apparent that changes in $\delta^{18}O_P$ at Lochnagar respond to multiple forcing agents to a lesser extent to than at Wallingford.

Table 4.9: Lochnagar regression models according to different selection criteria. BStep refers to backwards stepwise selection (Venables and Ripley 2002), FStep refers to forwards stepwise selection (Venables and Ripley 2002), best subsets refers to best subsets regression (Miller 2002). c = number of model components; T = monthly mean daily air temperature (K); P = monthly mean daily precipitation amount (mm), FW = monthly mean daily westerly flow velocity (hPa).

SITE: Lochnagar		
$n = 44$		
Method	**Model**	**R^2**
BStep	T	0.419
FStep	T	0.419
Best subsets (c=2)	T	0.419
FINAL MODEL	**$\delta^{18}O_P = 0.23T - 73.46$**	

LOCHNAGAR

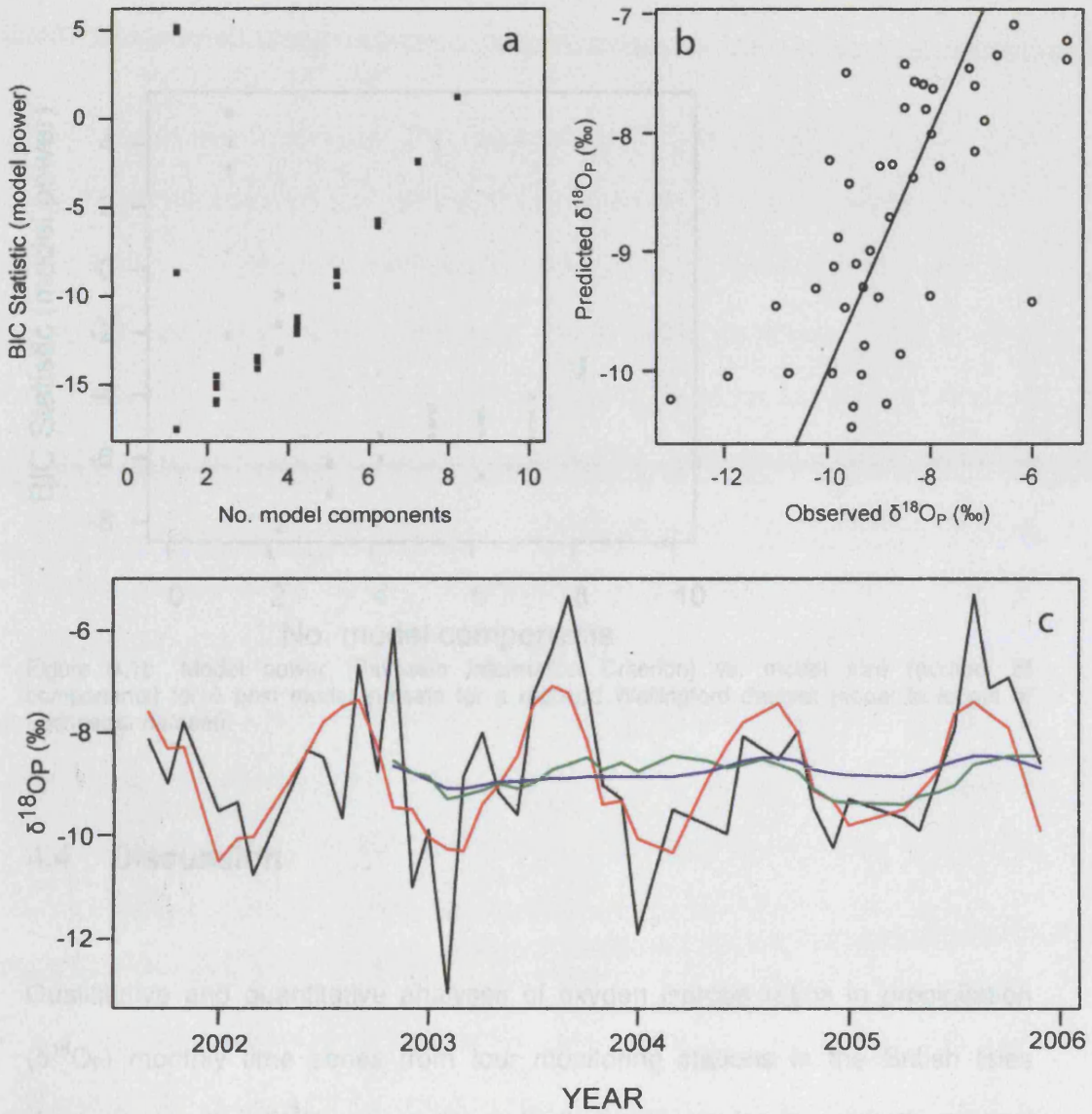

Figure 4.17: Multiple regression plots for Lochnagar $\delta^{18}O_P$ data, using final model in Table 8. (a) Model power (Bayesian Information Criterion) vs. model size (number of components) for 5 best model subsets; (b) Observed vs. predicted $\delta^{18}O_P$; (c) Comparison of observed (black line) and predicted (red line) monthly $\delta^{18}O_P$. Green line = annual running mean of observed data and blue line = annual running mean for predicted values.

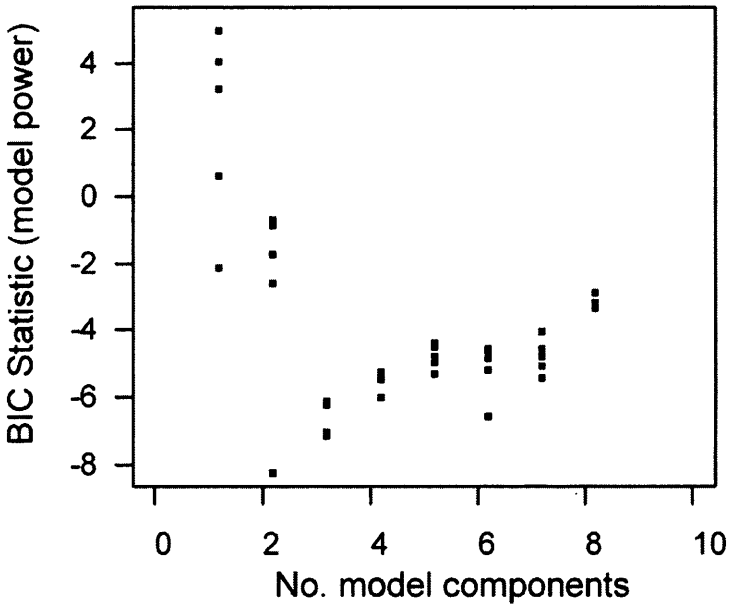

Figure 4.18: Model power (Bayesian Information Criterion) vs. model size (number of components) for 5 best model subsets for a reduced Wallingford dataset (equal to length of Lochnagar dataset).

4.4 Discussion

Qualititative and quantitative analyses of oxygen isotope ratios in precipitation ($\delta^{18}O_P$) monthly time series from four monitoring stations in the British Isles demonstrates that $\delta^{18}O_P$ responds markedly to climate forcing at both regional and local scales. In accordance with theoretical models and previous empirical observations from mid-latitude regions (e.g. Dansgaard 1964; Rozanski *et al.* 1993; Araguas-Araguas *et al.* 2000), all four monthly $\delta^{18}O_P$ records are significantly correlated with local air temperature, with reasonably consistent coefficients of 0.25 (Wallingford), 0.24 (Valentia), 0.28 (Keyworth) and 0.23 (Lochnagar), causing distinct seasonal cyclicity. At three of the four stations

studied (excluding Lochnagar) $\delta^{18}O_P$ is also significantly negatively correlated with precipitation amount (*P*). This response of $\delta^{18}O_P$ to precipitation amount has been well documented, and described previously for the British Isles by Darling and Talbot (2003). Both 'temperature' and 'amount' effects concur with the Rayleigh isotope distillation model of the physical controls on $\delta^{18}O_P$ at a particular site. The oxygen isotope composition of water vapour in an air mass is a function of the initial isotope composition of the evaporated water vapour, the degree of subsequent rain out prior to condensation at the monitored site, the amount of rain out at the site of collection and the thermodynamic conditions within the cloud at the point of condensation (Dansgaard 1964). Assuming a constant source and flux of water vapour evaporating from the surface ocean, leading to a constant initial $\delta^{18}O$ of the air mass, it is reasonable to expect that a large proportion of the variability in $\delta^{18}O_P$ at a particular site will be a function of air temperature, which controls both the amount of prior rain out over the ocean and the equilibrium fractionation between vapour and liquid water in the cloud, and precipitation amount (describing the extent of rain out at the sampling site). However, the assumption of constant moisture source and source conditions is weakly founded. In particular, variability in the source and trajectory of an air mass prior to condensation and precipitation above a certain location is extremely varied and is likely to result in changes in $\delta^{18}O_P$. The effect of such circulation processes was investigated here using air flow indices (the Jenkinson indices) as proxies for the source, trajectory and type of precipitation-bearing weather. For three of the four studied records – those which consist of > 10 years

monitoring data (Wallingford, Valentia and Keyworth), small but statistically significant effects of regional scale air flow circulation are apparent. For the Wallingford and Valentia datasets, the effect of air flow circulation on $\delta^{18}O_P$ is manifest through the index *FW* (westerly flow velocity), which in turn is highly correlated with the North Atlantic Oscillation index (NAO) (Tables 4.2 and 4.3; Figure 4.13). Changes in the strength of westerly flow and the orientation of the North Atlantic pressure field (as indicated by the NAO index) will influence the oxygen isotope composition of precipitation through both changes in the source of atmospheric moisture, affecting the initial isotope composition of the vapour prior to precipitation, and changes in the flux of atmospheric water vapour, influencing the relative effect of rain out processes.

The relative influence of *FW* appears inversely proportionate to the effect of *P*, according to the site location. For example, changes in $\delta^{18}O_P$ at Valentia are less responsive to *P* than at Wallingford or Keyworth. At Valentia, precipitation amount is high but the variability in precipitation amount is relatively low (Valentia mean monthly precipitation = 130 mm, monthly standard deviation = 67 mm). By comparison, Wallingford mean monthly precipitation amount is low, yet the relative variability is high (Wallingford mean monthly *P* = 50 mm, monthly standard deviation = 30 mm). At Valentia, which is situated on the coast, atmospheric moisture loss between the oceanic source and site of precipitation is low and therefore potential rain-out effects influence $\delta^{18}O_P$ to a lesser extent. As a consequence, at Valentia the source of the moisture and its initial oxygen

isotope composition (as partly indicated by *FW*) has a greater influence on $\delta^{18}O_P$. Further inland the inverse applies: at Wallingford and Keyworth, where precipitation events are less frequent and of lower magnitude, the degree of rain out prior to condensation and precipitation at the station exerts greater influence over both the amount and occurrence of precipitation and over $\delta^{18}O_P$. Consequently, the effect of *P* is greater and moisture source and trajectory are less important.

Keyworth is situated in the rain shadow of the Cambrian Mountains (Wales) and Pennine Hills, which lie to the west. As a result, changes in the westerly flux of moisture exerts a weaker control over precipitation amount and $\delta^{18}O_P$. Instead, at Keyworth, the frequency of southerly flow (*S*) plays a more important role, with a small but significant inverse relationship with $\delta^{18}O_P$. According to principal components analysis, *S* positively co-varies with the frequency of south-easterly and easterly air flows, indicating air mass trajectories from continental Europe (Figure 4.13). Continental weather brings with it isotopically depleted atmospheric vapour leading to a decrease in $\delta^{18}O_P$, as observed at Keyworth.

4.4.1 $\delta^{18}O_P$ at Lochnagar

Interpretation of $\delta^{18}O_P$ at Lochnagar is limited by the short record currently available for this site. However, when comparing Lochnagar $\delta^{18}O_P$ and a reduced dataset for Wallingford of equal length, notable dissimilarities are evident.

Multiple regression of Lochnagar $\delta^{18}O_P$ highlights only one variable, *T*, to explain $\delta^{18}O_P$. The lack of further explanatory variables is partly expected as a consequence of the short record length, however a dataset of equal length from Wallingford clearly demonstrates the significant influence of both temperature and precipitation amount. Consequently, it would appear that the processes driving $\delta^{18}O_P$ changes at Lochnagar differ to some extent from those at Wallingford. Seasonal temperature variability at Lochnagar is marked, ranging from – 7°C to 18 °C over the short monitoring period. Furthermore, it is possible that precipitation amount effects are less pronounced at Lochnagar due to marked rain shadow and altitude effects considerably draining moisture prior to precipitation at the site. A fuller understanding of the processes affecting $\delta^{18}O_P$ change at Lochnagar requires further extension of the monitoring record. In particular, it would appear that the effect of air temperature on $\delta^{18}O_P$ varies throughout the dataset – with $\delta^{18}O_P$ and air temperature most strongly associated during the relatively dry period between January 2003 and June 2004. During the periods where precipitation was higher, the inter-seasonal amplitude of $\delta^{18}O_P$ was lower and the time series more stochastic. It is possible, therefore, that the effect of air temperature at Lochnagar is mediated by other parameters, such as precipitation amount, possibly related to changes in atmospheric moisture content and relative humidity.

4.4.2 Comparing empirically modelled and observed $\delta^{18}O_P$

In order to interpret reliably palaeo- records of past $\delta^{18}O_P$ as records of past climate change, a strong quantitative understanding of the controls of $\delta^{18}O_P$ is vital. Quantitative models for monthly $\delta^{18}O_P$ improve palaeoclimate interpretation whilst highlighting the proportion of variance which can not be explained by simple climatic parameters. Despite the multitude of empirical studies into local and global controls over $\delta^{18}O_P$ patterns, few have taken a multiple regression approach to explain monthly scale variability (Yurtsever and Gat 1981; Liebminger *et al.* 2006). In this study, a marked improvement in predictive ability was achieved by using multivariate models over models based on individual variables such as temperature and precipitation amount. The most effective models derived were those for Valentia and Wallingford, where long monitoring records are available. Less success was achieved in modeling $\delta^{18}O_P$ for Keyworth and Lochnagar which have shorter data-sets.

Comparison between modelled and observed $\delta^{18}O_P$ for all sites identified marked outliers and considerable unexplained residual variance (Figures 4.14-4.17). In most cases, the models failed to capture extremes in winter $\delta^{18}O_P$ minima and summer $\delta^{18}O_P$ maxima. Such disagreements between modelled and observed data probably highlight the effects of forcing agents outside the set of explanatory variables explored in this study.

The occurrence of low $\delta^{18}O_P$ values during winter months that are not captured by the empirical models may be explained by variation of the type of precipitation – i.e. rain, hail or snow. At Lochnagar, the effect of heavy winter snowfall is marked in the $\delta^{18}O_P$ time-series. For example, the marked negative peak in $\delta^{18}O_P$ towards the end of 2002, is clearly related to a dominance of snowfall at this time, with surface snow values very similar to those for total precipitation (Figure 4.6). $\delta^{18}O$ values of snow water are believed to preserve the in-cloud formation conditions by limiting isotope exchange between precipitation and atmospheric vapour during precipitation fall, and can therefore be expected to reflect temperatures cooler than usual (Facy *et al.* 1963; Dansgaard 1964). There are no data for snow amount and snow $\delta^{18}O$ values for Wallingford, Valentia and Keyworth, since the precipitation collectors do not discriminate solid or liquid precipitation. Nevertheless, it is possible that similar snowfalls are also responsible for the marked negative events in $\delta^{18}O_P$ in these records.

Marked summer $\delta^{18}O_P$ maxima are also notable in all records and are not captured by model predictions. Increases in $\delta^{18}O_P$ would suggest warmer condensation temperatures or the influence of ^{18}O enriched atmospheric vapour, typical of low latitudes. However, coincidental changes are not evident in air temperature and atmospheric circulation parameters. One possible explanation is the evaporation of rain drops between the cloud base and ground level. Such effects have been frequently observed in more arid regions (e.g. Friedman *et al.*

2002b) and lead to marked increases in $\delta^{18}O_P$ by the preferential evaporation of the lighter ^{16}O molecule.

4.5 Conclusion

The local and regional scale variables controlling monthly and annual scale $\delta^{18}O_P$ changes at four sites in the British Isles were investigated using multivariate numerical analyses. Empirical models, based on multiple variables, can lead to a marked improvement over the simple univariate models commonly applied to palaeoclimate interpretation. Much of the variance in monthly $\delta^{18}O_P$ in the British Isles can be explained as a function of air temperature (*T*) and precipitation amount (*P*), which conform with Rayleigh distillation of atmospheric vapour (Dansgaard 1964). In addition, the effects of circulation indices, proxies for the more complex patterns in moisture source, air mass trajectory and weather type, can be observed, albeit to a very small extent. The $\delta^{18}O_P$ response to meteoric forcing agents, however, is not geographically uniform – even within the relatively small scale of the British Isles. In particular, $\delta^{18}O_P$ at Lochnagar appears less susceptible to changes in precipitation amount and air mass trajectory than the lower altitude sites. Although the $\delta^{18}O_P$ timeseries for Lochnagar is relatively short, air temperature appears to be the dominant control at this site – a potentially valuable observation with regards the use of oxygen isotope ratios to reconstruct past climate. By comparison, $\delta^{18}O_P$ at Valentia, is more susceptible to changes in air mass trajectory, whereas $\delta^{18}O_P$ at the inland sites of Wallingford

and Keyworth is controlled to a greater extent by precipitation amount, in addition to air temperature. Therefore, it appears that the effects of circulation type appear to diminish with distance from the coast and with altitude. Such geographic non-uniformity must be an important consideration in the use of isotope records in tracing past climate and in the comparison between coarse scale model outputs and localised isotope records.

In all cases, roughly 50% of the variance in monthly $\delta^{18}O_P$ is not explained. A portion of this unexplained variance can be accredited to marked summer and winter peaks, possibly due to the infrequent occurrence of snow formation in winter and rain drop evaporation in summer. These processes require further investigation. Further unexplained variance may result from factors such as changes in the vertical velocity of air masses, the altitude and exact temperature of precipitation formation, variations in the positioning of cyclonic foci with regard to the site of precipitation and variability in moisture source sea surface conditions (Gedzelman and Arnold 1994; Lawrence and Gedzelman 1996). In addition, monthly samples represent an amalgamation of various events during a month, and use of monthly average climate data may result in the loss of relevant information (Celle-Jeanton *et al.* 2001; 2004; Treble *et al.* 2005). Consequently, although the use of multivariate empirical models, including the effects of circulation patterns, can lead to a marked improvement in the interpretation of palaeo- $\delta^{18}O_P$, further work is required to investigate the considerable amount of variance not explained by simple climate indices, with greater attention paid to

changes over geographic space and short timescales. Modelling the response of long term $\delta^{18}O_P$ is problematic, and the processes which explain short term variability can not simply be extrapolated to account for long term changes due to the stochastic nature of short term precipitation amount patterns. Such questions are probably best addressed using annually resolved archives of $\delta^{18}O_P$, such as tree ring records and ice cores. It is evident that $\delta^{18}O_P$ changes are strongly related to meteorological processes, supporting their use in palaeoclimate research. However, future efforts are required to investigate the ability of general circulation models to predict localised, short term changes in $\delta^{18}O_P$ – both as a means for investigating past and present climate and atmospheric isotope hydrology.

Chapter 5:

Oxygen isotope ratios of lake and catchment waters at Lochnagar

5.1 Introduction

In temperate Europe the sediments of high altitude lakes are of major interest in palaeoclimate research, where anthropogenic modification of lake catchments has been minimal and where small catchments and marked seasonality can amplify the limnological response to climate change (Battarbee *et al.* 2002; Chapter 1). Oxygen and hydrogen isotope ratios of authigenic components, such as diatom silica or aquatic cellulose produced in such freshwater lakes can provide valuable archives of past climate change by reflecting changes in the isotope composition of precipitation (Edwards *et al.* 1996; von Grafenstein *et al.* 1996; 1999; Teranes and McKenzie 2001). There has been limited detailed research, however, into the relationship between isotope ratios of precipitation and those in lake waters (Darling 2004). This is especially important in small, high altitude lakes, where lake water isotope ratios can vary considerably with seasonally variable precipitation inputs (Yurtsever and Gat 1981) and alternating rain and snow fall (Neal *et al.* 1997).

The theory of lake isotope hydrology is well established (for detailed reviews, see Dincer 1968; Gonfiantini 1986; Gat 1995; Criss 1999), permitting numerous applications in

modelling the surface and groundwater hydrology of high latitude and altitude lakes (Krabbenhoft *et al.* 1990; Gibson 2001; Gibson *et al.* 2002). Due to logistical constraints, however, only a few have investigated the short-term variability in the isotope hydrology of such lakes (e.g. Gibson *et al.* 1996; Gibson 2002; Noon *et al.* 2002). Consequently, many isotope studies have relied on tracing average, long-term water balance conditions using models which assume isotopic and hydrologic steady state (Gibson 2002). The rapid climate and hydrological changes between seasons at high altitude and latitudes, however, means that equilibrium conditions are rarely achieved on an annual scale (Gibson 2002).

The response of a lake to changing isotopic composition of input depends largely on its hydrological setting – specifically the residence time between water entering and leaving the lake (Gat 1995). Residence time is strongly affected by the size of the reservoir, so that large reservoirs such as groundwater fed and large volume lakes are seasonally more stable than small reservoirs fed predominantly by precipitation or surface waters (Gat 1995). Seasonal changes in stratification can add further complexity (Gat 1970; Benson and Paillet 2002; Gibson *et al.* 2002) and in some cases formation of ice can lead to isotopic fractionation of lake waters by the preferential removal of heavy isotopes (Friedman and Redfield 1958; Ragotzkie and Friedman 1965; Krabbenhoft *et al.* 1990).

In this chapter, the results of intensive monitoring of the isotope hydrology of Lochnagar are analysed in order to assess the processes which affect the transfer of $\delta^{18}O_P$ signals to lake waters. Previous research in the Scottish uplands has studied the isotope hydrology of precipitation, groundwater and fluvial systems (Kay *et al.* 1984; Soulsby *et*

al. 2000; Rodgers *et al.* 2005) but this is the first study of lake waters in the region. Water input to Lochnagar is derived from three sources – direct precipitation to the lake, catchment runoff and throughflow via glacial and peri-glacial regolith, soils and fractured bedrock. The fractured nature of the catchment granite suggests that groundwater seepage from a perched aquifer is unlikely. Low infiltration and rapid catchment runoff would indicate that recent precipitation accounts for the overwhelming majority of lake input (Jenkins *et al.* 2001), except for storage and periodic release of melted snow. The catchment is generally snow-covered over the winter months, usually until early May, however snow patches can remain in steep, sheltered gullies until July.

5.2 Data analysis methods

Meteorological data collection and sampling and analyses of lake, catchment and rain waters for oxygen isotopes are described in Chapter 3 (Sections 3.1.1 - 3.1.3). Bi-weekly measurements were collected between May 2000 and September 2005.

5.2.1 Calculation of evaporation and thermal (stratification) index

Evaporation values were calculated using the model of Penman (1948; eqs. 1, 2), modified by Linacre (1992) (c.f. Jones *et al.* 2005):

$$E = [0.015+4.10^{-4}T+10^{-6}z].[480(T+0.006z)/(84 - A) - 40+2.3u(T-T_d)] \quad (1)$$

where E = evaporation (mm/day), T = air temperature (°C), z = altitude (m), A = latitude, u = windspeed, and T_d is dew point temperature, defined by Linacre (1992) as:

$$T_d = 0.52\ T_{min} + 0.60\ T_{max} - 0.009\ (T_{max})^2 - 2°C \quad (2)$$

where T_{min} and T_{max} are minimum and maximum air temperatures respectively.

From lake water temperature data, a lake thermal index (TI) was calculated as:

$$TI = T_{1.5} - T_{19} \quad (3)$$

where the numbers in subscript represent the depth of lake water temperature measurements. TI indicates the degree to which lake waters are stratified or well mixed: where waters are mixed the value is around zero; positive values indicate conventional stratification, with a warmer epilimnion; negative values indicate inverse stratification, with the hypolimnion warmer than the epilimnion.

5.2.2 Water and isotope mass balance and lake water residence time

Lake isotope hydrological models can significantly improve palaeoclimate interpretation of sediment oxygen isotope profiles by allowing the effects of hypothetical climate changes to be simulated and compared to palaeo- data (e.g. Ricketts and Johnson 1996; Benson and Paillet 2002; Jones *et al.* 2005). The isotope mass balance of a lake, assuming negligible groundwater and evaporation flux, is solved by Gat (1995) as:

$$\Delta\delta^{18}O_L = (IN/V).(\delta^{18}O_P - \delta^{18}O_L) \quad (4)$$

where $\Delta\delta^{18}O_L$ is change in the oxygen isotope composition of lake water ($\delta^{18}O_L$) and V is lake water volume. In order to obtain a continuous time series of $\delta^{18}O_P$ with sampling intervals equal to measured $\delta^{18}O_L$ for the modelling exercise, missing values in the $\delta^{18}O_P$ data were bridged by linear interpolation. IN is the total input volume for the isotope sampling period, calculated as:

$$IN = P + S_i \quad (5)$$

where P is direct precipitation to the lake surface (precipitation in m (p) x lake surface area) and S_i is surface runoff estimated as:

$$S_i = p.\ CA.\ k \quad (6)$$

where CA is catchment area and *k* is a runoff coefficient, estimated for Lochnagar as 0.9 (Jenkins *et al.* 2001).

Residence time in days (RT) was calculated as:

$$RT = V / (IN/days) \quad (7)$$

where *days* is the length of time in days between sample collections.

For the purpose of model sensitivity tests for differing input/volume (IN/V) scenarios, $\delta^{18}O_P$ was simulated as a sine wave of mean *u*, equal to the average values for Lochnagar $\delta^{18}O_P$ over the whole sampling period:

$$\delta P_{\sin} = u - \sin\left(\frac{t}{w}\right) \tag{8}$$

where *t* is time in radians, with calendar days normalised so that 1 year is equal to 6.28 radians and *w* is a radial function defined as:

$$w = \frac{1}{\left(\frac{\pi}{180}\right)} \tag{9}$$

In order to quantify the shift in phase lag and amplitude between $\delta^{18}O_P$ and modelled $\delta^{18}O_L$, sine waves were fitted to the model output as (c.f. Soulsby *et al.* 2000):

$$\delta L_{\sin} = u + \left(A.\sin\left(\frac{\theta - t}{w}\right)\right) \tag{10}$$

where *A* is the amplitude of modelled $\delta^{18}O_L$ (equation 4) and θ is the phase lag in radians determined by trial and error until linear regression between modelled $\delta^{18}O_L$ and δL_{sin} produced an R_2 of 1.

5.3 Results

5.3.1 Seasonal meteorological variability, 2001-2005 (Figure 5.1)

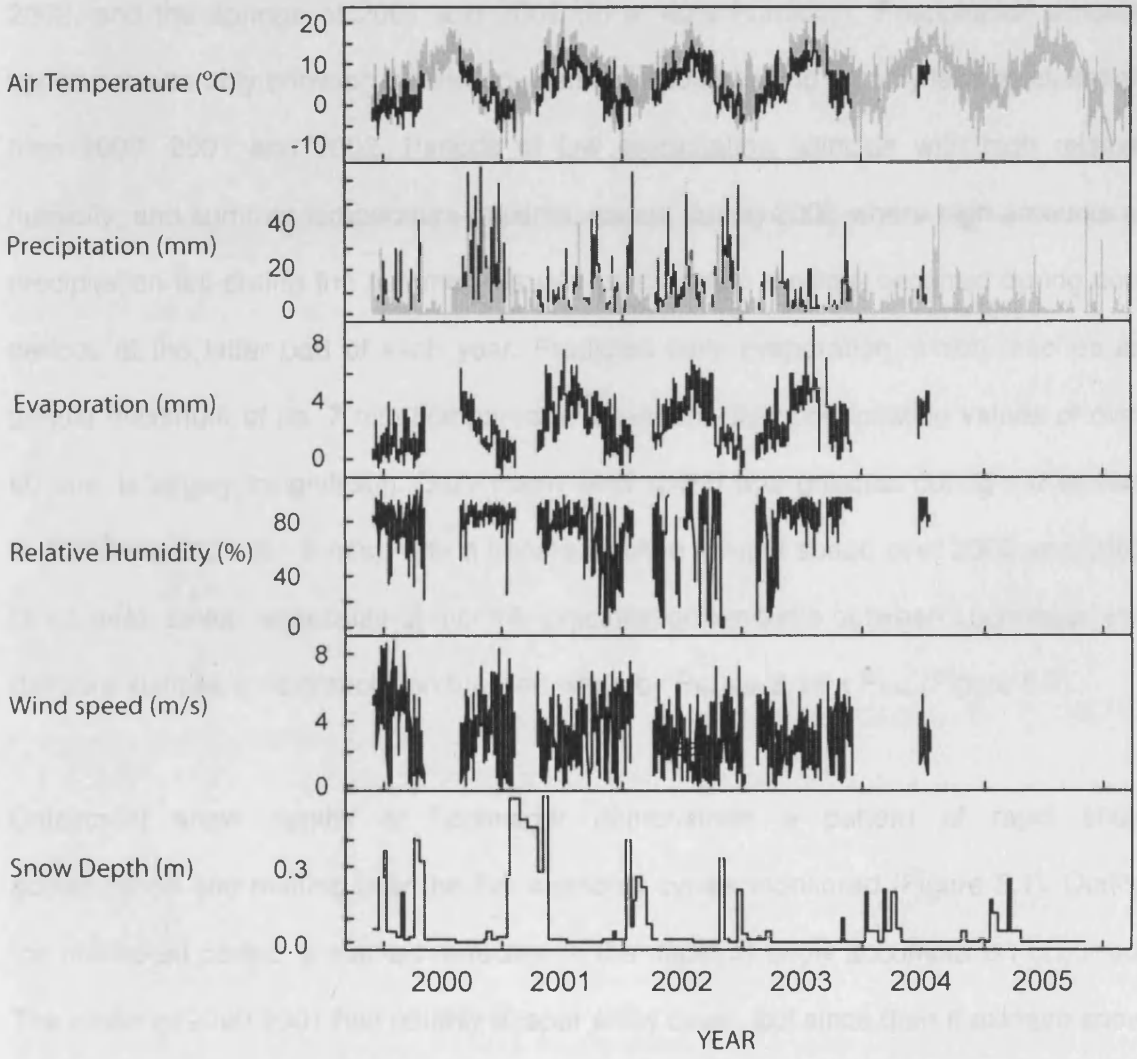

Figure 5.1: Meteorological data for Lochnagar (black lines) and Balmoral (grey lines, air temperature and precipitation amount only) over isotope sampling period. Evaporated was calculated using equations 1 and 2. Gaps in the time series represent periods where no data was collected at Lochnagar, however snow depth is a continuous series and zero values represent absence of snow within the catchment.

Maximum daily mean air temperatures (c. 15°C) occurred at Lochnagar between June-August with little variation over the monitored period, except for a notably warm period

during the late summer of 2003 (20°C). Similarly, there was only a moderate shift towards higher temperature minima over the period. Relative humidity was generally high throughout (80-100%) except for notable declines during the autumns of 2001 and 2002, and the springs of 2001 and 2002 (to c. 40% humidity). Precipitation amount varied considerably between monitored years with 2003 having notably less precipitation than 2000, 2001 and 2002. Periods of low precipitation coincide with high relative humidity, and summer temperature maxima, except during 2002 where high amounts of precipitation fell during the summer. Usually precipitation maxima occurred during cool periods at the latter part of each year. Predicted daily evaporation, which reaches an annual maximum of ca. 7 mm compared to maximum daily precipitation values of over 60 mm, is largely insignificant. Daily mean wind speed was greatest during the winters of 2000 and 2001 (6 - 8 m/s), with a general decline in wind speed over 2002 and 2003 (1 - 5 m/s). Linear regression of monthly precipitation amounts between Lochnagar and Balmoral defines an extrapolation function whereby $P_{NAG} = 2.14 \times P_{BAL}$ (Figure 5.2).

Catchment snow depths at Lochnagar demonstrate a pattern of rapid snow accumulation and melting over the five seasonal cycles monitored (Figure 5.1). During the monitored period, a marked reduction in the depth of snow accumulation occurred. The winter of 2000-2001 had notably deeper snow cover, but since then maximum snow depth has declined, the duration of the snow cover period decreased and the period of snow cover has become less continuous.

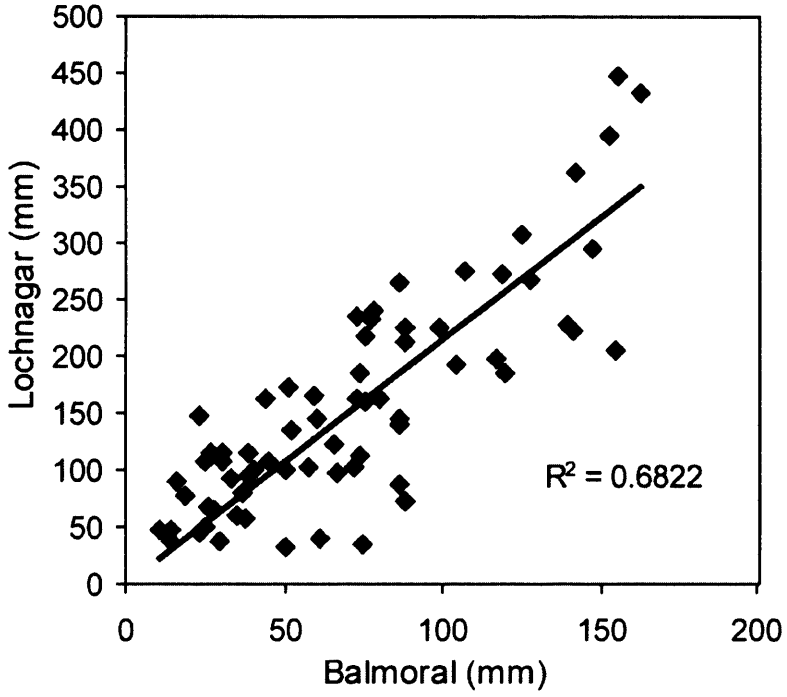

Figure 5.2: Comparison of monthly precipitation amount (mm) between Lochnagar (P_{NAG}) and Balmoral (P_{BAL}) from September 1996 to October 2003, to enable extrapolation between the two. Linear regression slope = 2.14, intercept = 0 (fixed), R^2 = 0.6822.

5.3.2 Lake stratification and ice cover patterns (Figure 5.3)

Ice formed on the lake surface in December/early January for all the years monitored. In 2001 ice-out occurred in mid-May, however during 2002-2005 the ice was gone by the end of April. In early December 2004, ice formed on the lake briefly before melting completely and re-freezing later in the month. Ice thickness markedly declined over the five years, with maximum thickness of c. 300 mm in 2001 and 2002, 200 mm in 2003 and 100 mm in 2004.

Periods of lake mixing (TI ≈ 0) are most prominent during autumn, following summer stratification (TI > 0) (Figure 5.3). Stratification and surface warming is most marked in 2003, and prominent in 2000 and 2001. During 2002 however, the stratification period was fragmentary, and consequently the epilimnion did not warm considerably with respect to the hypolimnion. Inverse stratification (TI < 0) occurred during winter periods coinciding with lake surface ice cover (Figure 5.3). During the springs of 2001 and 2002, following the ice melt, the shift from inverse stratification to conventional stratification was almost instantaneous. In 2003 and 2004, however, a period of lake water mixing occurred prior to positive stratification.

5.3.3 $\delta^{18}O$:$\delta^{2}H$ covariance (Figure 5.4)

As shown before in Chapter 4 (Figure 4.7), the bi-plot of $\delta^{18}O$:$\delta^{2}H$ in rain waters at Lochnagar defines a local meteoric water line (LMWL) of gradient 7.8, similar to the Global Meteoric Water Line, which has a gradient of 8 (Craig 1961) (Figure 5.4). Snow waters plot away from this line, particularly at high δ values, with a gradient of 8.8 (Figure 5.4a). Lake inflow and lake waters have a shorter range of variability, and appear to cluster strongly about the LMWL. At closer inspection, however, both inflow and lake water values plot above the GMWL (Figure 5.4b). Inflow δ values define a gradient of 7.2 (IWL), whereas the gradient of 5.7 for lake water is notably lower (LWL). In both cases, the water line intercepts that of precipitation in the upper range of values (~ –6‰ for inflow, ~ –8‰ for lake) with greatest deviation from precipitation at the lowest values ($\delta^{18}O_L$ < –9‰) (Figure 5.4b). Since $\delta^{18}O$ and $\delta^{2}H$ values are so closely related, all subsequent discussion will relate solely to $\delta^{18}O$.

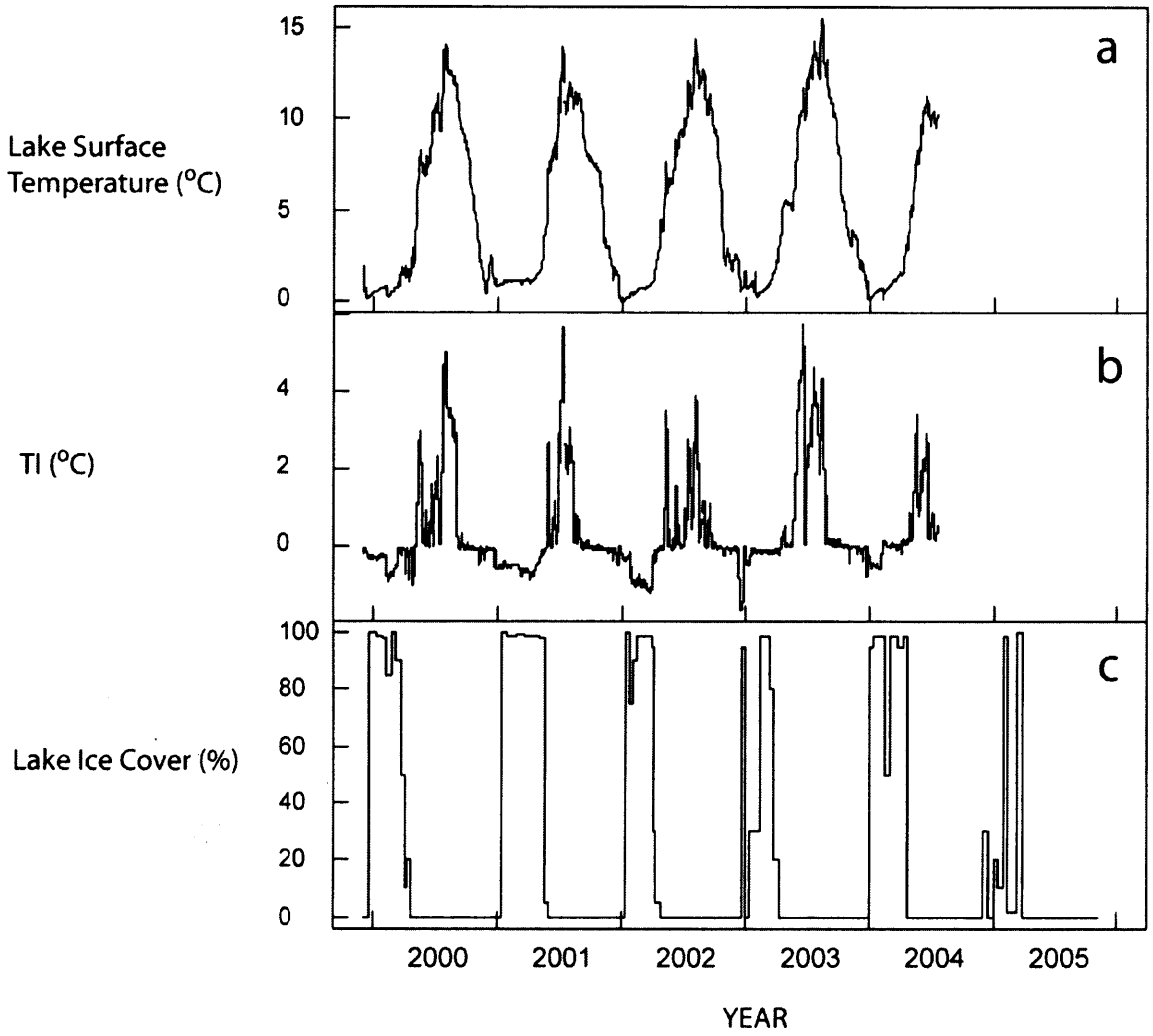

Figure 5.3: Lake surface temperature (a), mixing – as shown by thermal index (TI) (b) and ice cover changes (c) in Lochnagar over sampling period.

5.3.4 Seasonal isotope ratios in precipitation

Oxygen isotope ratios in precipitation ($\delta^{18}O_P$) at Lochnagar between August 2001 and September 2005 vary considerably on an intra- and inter-annual basis (Chapter 4). The time series (Figure 5.5) shows a roughly sinusoidal pattern with annual $\delta^{18}O_P$ maxima of

around –6‰ occurring in summer and winter minima of ca. –11‰. Short term fluctuations away from this trend are evident however, most notably from October 2002 – May 2003, where $\delta^{18}O_P$ increased over the winter period. The amplitude of $\delta^{18}O_P$ seasonality increased from 2001-2003, but decreased in 2004.

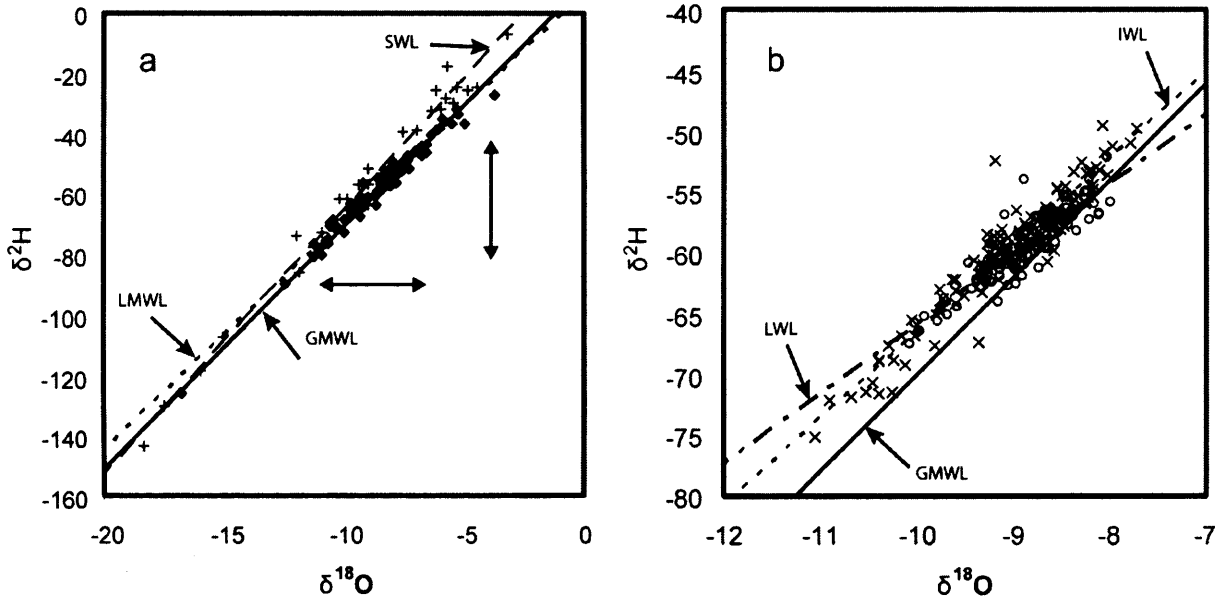

Figure 5.4: Bi-plots of $\delta^{18}O$ vs δD for meteoric and surface waters at Lochnagar. (a) Rain water (filled diamonds) and snow (vertical crosses). (b) inflow (diagonal crosses) and lake water (open circles). Water lines defined as: Rain water (local meteoric water line, LMWL) – n = 82, slope = 7.5, R^2 = 0.97; Snow (SWL) – n = 29, slope = 8.7, R^2 = 0.98; Inflow (IWL) – n = 108, slope = 7.1, R^2 = 0.91; Lake (LWL) – n = 137, slope = 5.8, R^2 = 0.81. Global meteoric water line (GMWL) slope = 8. Double ended arrows in (a) indicate range of axes in (b).

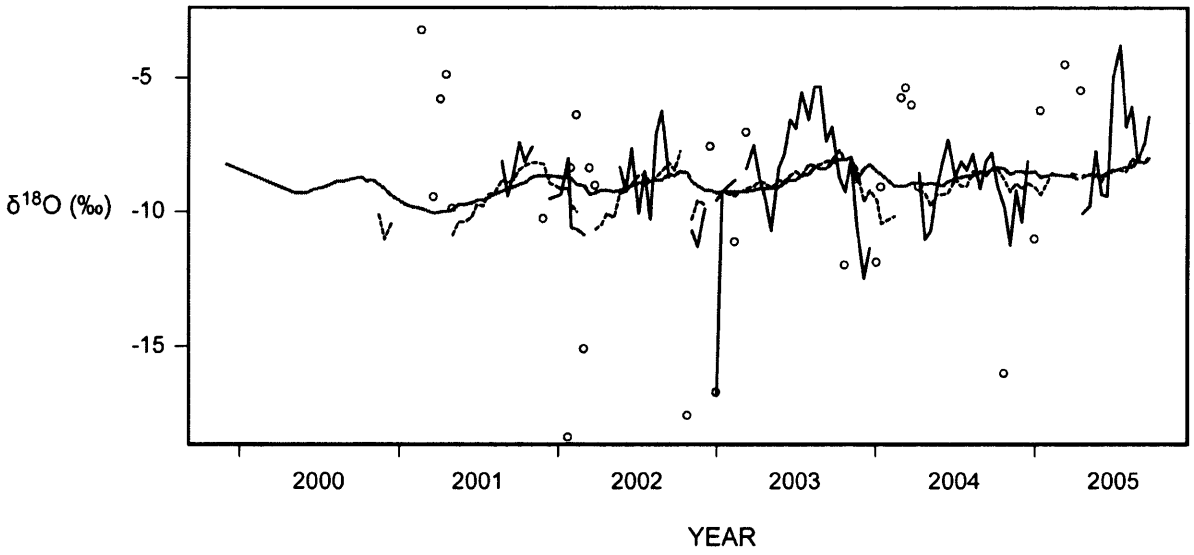

Figure 5.5: Combined time series for $\delta^{18}O$ in rain water (solid black line), snow (circles), inflow water (dotted black line) and lake water (solid grey line).

5.3.5 Catchment and lake water isotope ratios

The amplitude of seasonal $\delta^{18}O$ variability and the degree of noise about the general trend is markedly reduced between precipitation ($\delta^{18}O_P$) and lake inflow water ($\delta^{18}O_{IF}$) and again between inflow and lake waters ($\delta^{18}O_L$) (Figure 5.5). Over 2001-2002, and again during 2004, the isotope ratios in inflow waters were closely related to those of precipitation ($\delta^{18}O_{IF} \approx \delta^{18}O_P$), with a short lag time of 1-2 months, and little damping of the amplitude of variability (Figure 5.6). Over 2003 and 2005, marked increases in $\delta^{18}O_P$ were not manifest in $\delta^{18}O_{IF}$ and the time lag between the two summer peaks was greater (ca. 3-4 months). The correlation between $\delta^{18}O_L$ and $\delta^{18}O_{IF}$ also fluctuates with time (Figure 5.7). From January to November 2003 there was very little difference between the two, however between 2001 and 2002 summer $\delta^{18}O_{IF} > \delta^{18}O_L$ and in 2001 there was a notable time lag in $\delta^{18}O_L$. During most winters, $\delta^{18}O$ decreased markedly in

the inflow but not in lake water. This was least marked in the winter of 2002-03 and in 2004, it occurred earlier in the winter, and to a less marked extent.

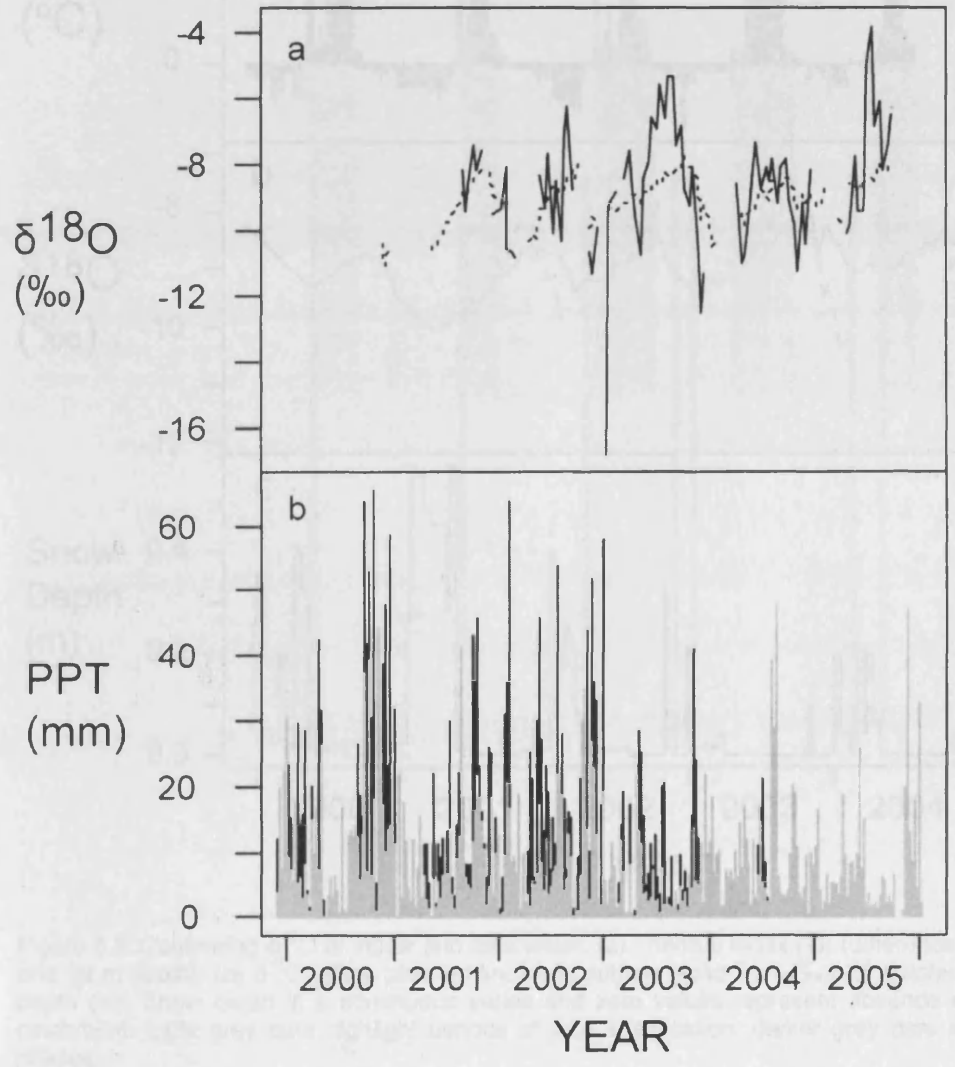

Figure 5.6: (a) Comparison between $\delta^{18}O$ of inflow water (dotted line) and precipitation (solid line) and (b) daily precipitation amount at Lochnagar (black bars) and Balmoral (grey bars). Gaps in the dataset represent periods where no data were collected.

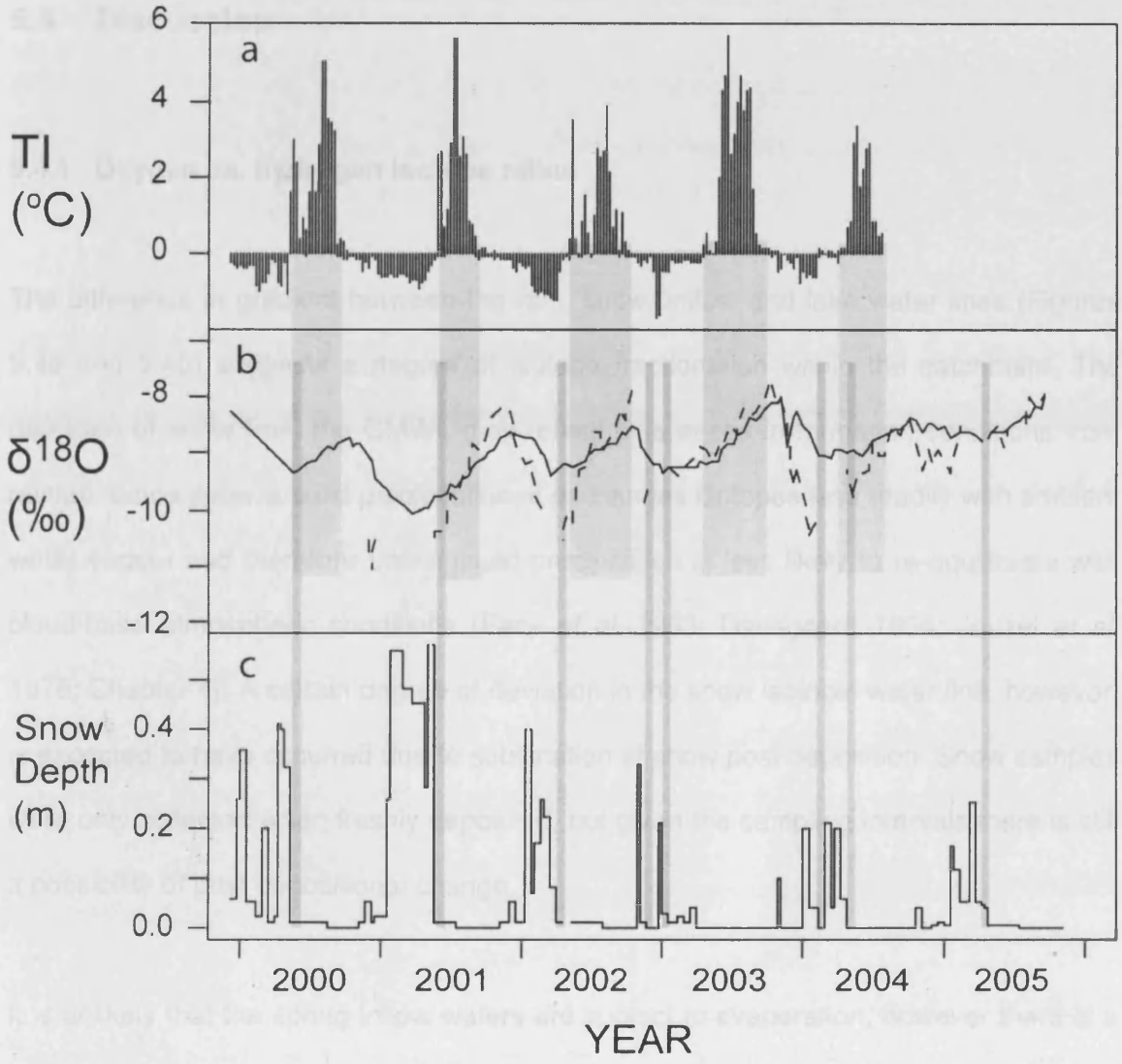

Figure 5.7: Comparing $\delta^{18}O$ of inflow and lake water. (a) Thermal index (TI) (difference in °C between 1.5 and 19 m depth); (b) $\delta^{18}O$ inflow (dashed line) and outflow (solid line) (‰); (c) catchment average snow depth (m). Snow depth is a continuous series and zero values represent absence of snow within the catchment. Light grey bars highlight periods of lake stratification; darker grey bars indicate snow melt phases.

5.4 Discussion

5.4.1 Oxygen vs. hydrogen isotope ratios

The difference in gradient between the rain, snow, inflow and lake water lines (Figures 5.4a and 5.4b) suggests a degree of isotope fractionation within the catchment. The deviation of snow from the GMWL may reflect differences in formation conditions from rainfall. Since snow is solid precipitation, it exchanges isotopes less readily with ambient water vapour and therefore unlike liquid precipitation is less likely to re-equilibrate with cloud-base atmospheric conditions (Facy *et al.* 1963; Dansgaard 1964; Jouzel *et al.* 1975; Chapter 4). A certain degree of deviation in the snow isotopic water line, however, is expected to have occurred due to sublimation of snow post deposition. Snow samples were only collected when freshly deposited, but given the sampling intervals there is still a possibility of post depositional change.

It is unlikely that the spring inflow waters are subject to evaporation, however there is a change in slope between rain waters and spring inflow (Figures 5.4a and 5.4b). One explanation for this difference might be that some of the inflow spring water also contains melted ice that forms between fissures in the rock face during winter months. There are large differences between precipitation and lake water $\delta^{18}O$, but not as a result of evaporation of lake water. This is evident because the majority of deviation from the GMWL occurs at lower δ values, which occur during the winter months. The difference may instead be a result of the formation of ice on the lake surface, since ice

preferentially incorporates heavier isotopes (Friedman and Redfield 1958). This phenomenon has been used to explain lower than expected δ^2H and $\delta^{18}O$ values in lake waters from Antarctic and high alpine lakes (Ragotzkie and Friedman 1965; Krabbenhoft *et al.* 1990).

5.4.2 Short term catchment and lake effects

Temporal changes in the degree of lag and amplitude reduction between $\delta^{18}O_P$ and $\delta^{18}O_{IF}$ reveal the effect of variable rates of water passage through the catchment (Figure 5. 6). During periods of high precipitation (e.g. during 2001-2002 and 2004), increased hydraulic pressure caused higher throughflow of water leading to a $\delta^{18}O_{IF}$ signal closely in phase with $\delta^{18}O_P$ and with only a minor reduction in amplitude. When precipitation was reduced during 2003, throughflow rate also declined and the seasonal $\delta^{18}O_{IF}$ signal became lagged (~12 weeks) and dampened with regards to $\delta^{18}O_P$ (Figure 5.6).

A similar process takes place where lake waters are concerned, with changes in residence time affecting the relationship between the isotope composition of input and lake water. Assuming constant lake water volume and surface runoff conditions, residence time is a function of precipitation amount. Mean residence time in Lochnagar was 254 days, however this varied markedly, with a maximum of 639 days (following low precipitation in March 2003) and a minimum of 56.7 days (following high precipitation in October 2002). Increasing residence time and decreasing throughflow rate leads to increased phase lag and increased amplitude reduction between $\delta^{18}O_P$ and $\delta^{18}O_L$ for example during much of 2003 (Figure 5.6).

The effect of further limnological processes can be observed by comparing $\delta^{18}O_{IF}$ and $\delta^{18}O_L$. In particular, $\delta^{18}O_L$ does not show the marked winter declines that are seen in $\delta^{18}O_P$ and $\delta^{18}O_{IF}$ (Figure 5.7). The difference is most likely the consequence of changes in lake stratification and mixing. During periods of stratification, the volume of water with which inflowing waters are mixed is markedly reduced. The net effect is that residence time between waters entering and leaving the lake is reduced, and input waters have a greater proportional effect on surface water values. During summer 2003 at Lochnagar, where lake stratification was most pronounced, $\delta^{18}O_{IF}$ and $\delta^{18}O_L$ were closely coupled (Figure 5.7: grey shaded area). In contrast, winter periods where changes in $\delta^{18}O_{IF}$ are not manifest in $\delta^{18}O_L$ coincide with inverse stratification of the lake, suggesting that cold input waters, including snow melt, sink to the bottom of the lake and are stored in the hypolimnion rather than quickly expelled. At the time of spring lake water overturn, the epilimnion is then fed by a flux of hypolimnetic water, which accumulated prior to the onset of stratification. This was clear in 2001 and 2002 for example, where marked differences in summer $\delta^{18}O_{IF}$ and $\delta^{18}O_L$ coincided with marked winter inverse stratification (Figure 5.7). During 2003 however, following a weak inverse stratification the preceding winter, the pattern did not occur. Although ice formation appears to have an effect on the slope of the $\delta^{2}H$:δ18O relationship (Figure 5.4), these effects are not apparent by visual inspection of the $\delta^{18}O_L$ time series (Figure 5.3).

Comparing $\delta^{18}O_{IF}$ and $\delta^{18}O_L$ also enables an assessment of the effects of snowmelt on $\delta^{18}O_L$ – where periods of high snowmelt should manifest in a divergence between $\delta^{18}O_{IF}$ and $\delta^{18}O_L$. The flux and isotope composition of snowmelt was not monitored at Lochnagar, however the timing of snowmelt phases is indicated by the rapid depletion of

catchment snow cover which occurred at the end of winter in all monitored years (Figure 5.7). Despite the loss of large volumes of snow from the catchment, snow depletion phases appear to have little effect on $\delta^{18}O_L$ during the monitored period (Figure 5.7: dark grey bars).

5.4.3 Model output

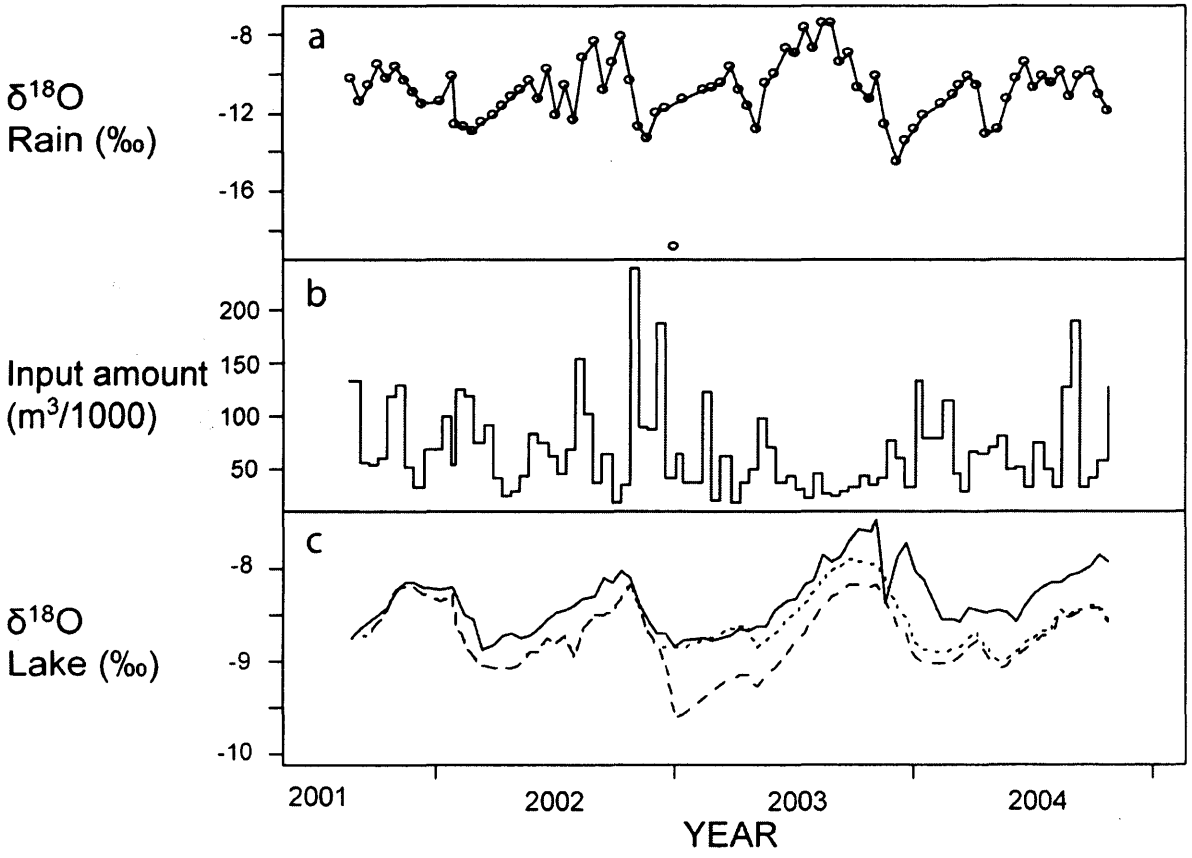

Figure 5.8: Isotope hydrological model (equation 4) inputs and outputs. (a) Oxygen isotopes in precipitation ($\delta^{18}O_P$): full dataset (circles) and excluding value for 01/01/2003 (solid line). (b) Predicted input from extrapolation of Balmoral precipitation combined with equations 5 and 6. (c) Oxygen isotopes in lake water: observed values (solid line), modeled values using full $\delta^{18}O_P$ dataset (dashed line) and modeled values using reduced dataset without value for 01/01/2003 (dotted line).

A comparison between modelled and observed $\delta^{18}O_L$ is limited to the period between August 2001 and September 2004 where $\delta^{18}O_P$ data overlap with available precipitation amount data from Balmoral (Figure 5.8). Modelled $\delta^{18}O_L$ based on the complete $\delta^{18}O_P$ dataset follows a similar pattern to observed $\delta^{18}O_L$. However, since the isotope mass balance model is additive, the long term projection for modelled $\delta^{18}O_L$ is liable to drift in response to anomalous individual input values. One notable example is the rain sample taken on 01/01/2003, where $\delta^{18}O_P$ = –16.8‰, the effect of which is clear when it is removed from the model input (Figure 5.8). This sample probably consisted predominantly of snow water, which was also sampled on the same date and had $\delta^{18}O$ = –16.7‰ (Figure 5.5). The model over-estimates the effect of this precipitation on lake water however, resulting in a marked divergence between modelled and observed $\delta^{18}O_L$. Two possible explanations for this divergence are: a) the precipitation event did not reach the lake water, either due to lake ice cover preventing infiltration to the lake or wind and sublimation removing the snow cover prior to melting; or b) the heavy rain that occurred at Balmoral did not occur at Lochnagar, such that the effects of the snow event prior to 01/01/2003 are over-weighted in the model. In reality it is likely that a combination of these effects took place, and may have occurred throughout the monitoring period. Such effects may explain the other inconsistencies between modelled and observed $\delta^{18}O_L$. Without more detailed data concerning lake outflow discharge, snow melt water volumes and vertical distribution of lake water oxygen isotopes, we are unable to fully model snow melt and stratification effects on surface water $\delta^{18}O_L$. However the overall similarity between modelled and observed $\delta^{18}O_L$ using equation 4 suggests that these effects have a lesser effect on the contemporary lake system.

Application of equation 4 to simulated $\delta^{18}O_P$ for differing IN/V scenarios (Figure 5.9) replicates the patterns observed at Lochnagar in Figures 5.6 and 5.7 – with high IN/V ratio caused by high precipitation amount or low effective volume (due to stratification) resulting in $\delta^{18}O_L$ values with an amplitude similar to $\delta^{18}O_P$ and little time lag between $\delta^{18}O_L$ and $\delta^{18}O_P$. Conversely, lower IN/V ratio leads to a marked lag effect and dampening of $\delta^{18}O_L$. For example – when annual precipitation equals roughly six times lake volume (IN/V ≈ 6), the amplitude of $\delta^{18}O_L$ is ~70% of $\delta^{18}O_P$ and the time lag is roughly 45 days. When IN/V ≈ 1, however, amplitude is reduced to 17% of $\delta^{18}O_P$ and $\delta^{18}O_L$ lags $\delta^{18}O_P$ by ~ 88 days. Figure 5.10 demonstrates that the difference in amplitude (dA) and the time lag (θ) between $\delta^{18}O_L$ and $\delta^{18}O_P$ are non-linear functions of the input/volume ratio (IN/V). Changes in IN/V are most influential over the seasonal structure of lake isotope hydrology at low IN/V values, and increases in annual precipitation input over 10 times the lake volume will have little further effect on the lag or amplitude dampening.

5.4.4 Importance for palaeoclimate research

$\delta^{18}O_P$ is a complex yet potentially valuable palaeoclimate tracer where past $\delta^{18}O_P$ values can be deduced from lake sediment records (Chapter 4). Mean annual oxygen isotope ratios of lake waters at Lochnagar are equal to the weighted mean annual values for precipitation at the site during the 5½ monitored years, indicating negligible effects of evaporation of surface waters or groundwater inputs to the lake. However, the same is not true for monthly values. Due to hydrological factors – such as precipitation driven

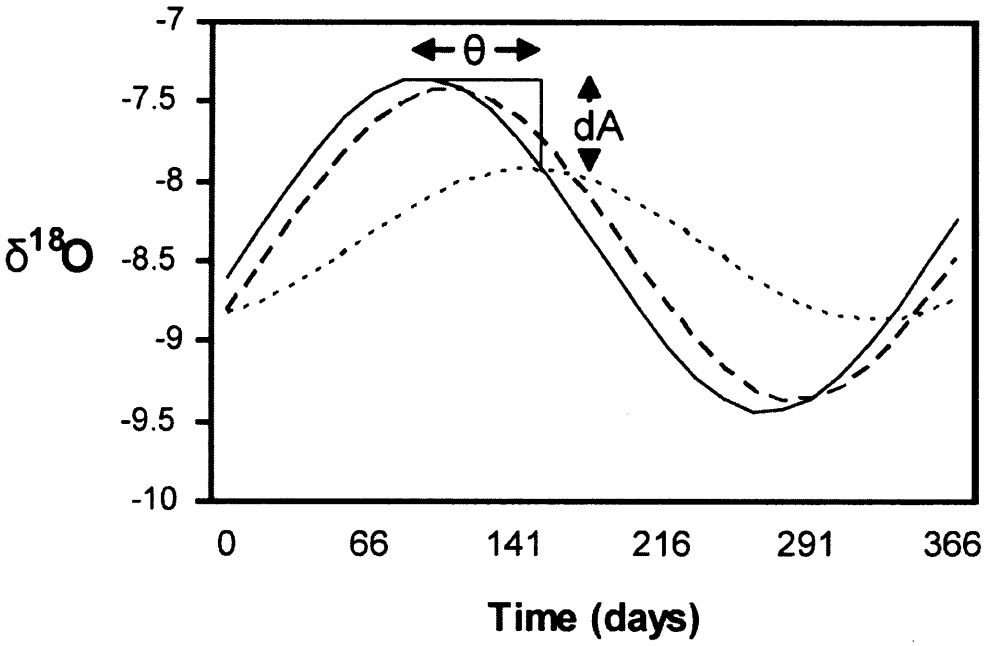

Figure 5.9: Isotope hydrological model outputs for different scenarios. Solid line = $\delta^{18}O_P$, dashed line = $\delta^{18}O_L$ when IN/V=12.5, dotted line = $\delta^{18}O_L$ when IN/V=3.125. Arrows illustrate definition of amplitude change (dA) and time lag (θ).

changes in lake water throughflow rate and residence time, and limnological factors – such as seasonal lake stratification, the seasonal pattern of $\delta^{18}O_L$ values does not reflect that of $\delta^{18}O_P$. Such effects are important since it is rare that authigenic and biogenic minerals or organic compounds (from which $\delta^{18}O$ and/or $\delta^{2}H$ can be measured) are produced in a lake evenly throughout the year. Furthermore, the seasonal pattern of lake water $\delta^{18}O$ values and the production of isotope bearing sediment components is unlikely to remain constant with time, in particular under changing climate regimes. Chapters 6 and 7 address this issue in greater detail.

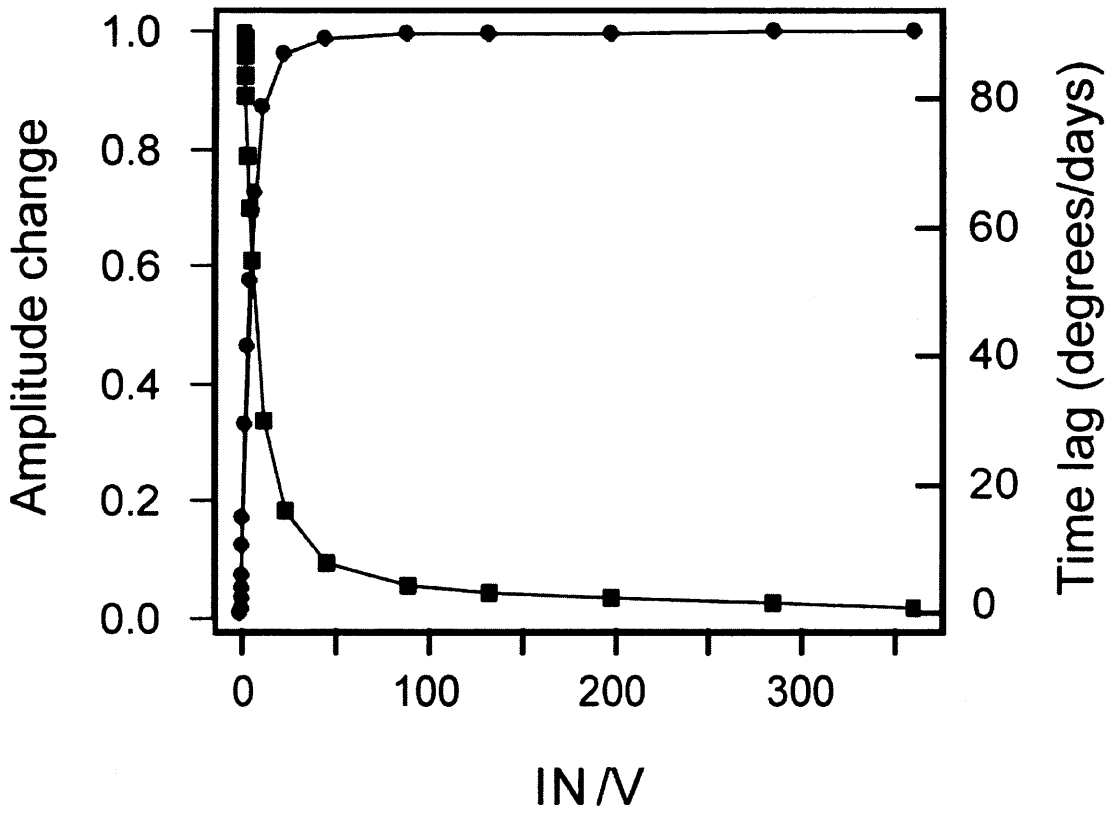

Figure 5.10: Predicted amplitude change (dA) and lag (θ) of $\delta^{18}O_L$ for variable IN/V scenarios, where IN = annual water input to the lake and V = lake water volume. Amplitude change (circles) expressed as fraction of the amplitude of $\delta^{18}O_P$. Lag (squares) expressed as time difference in degrees (days) between peaks in $\delta^{18}O_P$ and $\delta^{18}O_L$ (see Figure 9 for illustration). Solid lines represent smoothed interpolation.

5.5 Conclusion

Short term changes in the oxygen isotopic composition of lake surface waters at Lochnagar follow a seasonal pattern similar to that of the isotopes in local precipitation. Mediating this response, however, are changes in residence time, lake ice cover and lake stratification, which mean that the relationship between $\delta^{18}O_L$ and $\delta^{18}O_P$ is rarely linear. Where residence times are short (due to high precipitation or lake stratification)

$\delta^{18}O_L$ is closely related to $\delta^{18}O_P$, however when residence time increases (low precipitation or mixed lake) $\delta^{18}O_L$ resembles a time lagged and seasonally averaged $\delta^{18}O_P$. Therefore, in addition to the climatic controls over isotope ratios in precipitation, the manner in which lake waters reflect those of precipitation also vary with climate. A simple mass balance model reproduces much of the intra-annual variability in $\delta^{18}O_L$, suggesting that changes in precipitation amount is responsible for the majority of changes over the monitored period. The model enables changes to the seasonal structure relative to seasonal $\delta^{18}O_P$ (i.e. in the amplitude of $\delta^{18}O_L$ variability and the degree of time lag) to be predicted, where the input to lake volume ratios are known.

The implications of these observations are important for the use of $\delta^{18}O$ records in palaeoclimatology, in particular when considering the uneven nature of mineral synthesis and organic compound production over the annual cycle (see Chapters 6 and 7). Greater consideration of the spatial and temporal patterns of isotope ratios in lake waters is required if lake sediment records are to provide accurate records of past climate change.

Chapter 6:

Seasonal patterns in diatom abundance and taxonomic composition at Lochnagar

6.1 Introduction

6.1.1 Rationale

The physical conditions within a lake, and the isotope composition of lake water can vary considerably over short term seasonal timescales (Chapter 5). Equally variable over the seasonal cycle is the production rate of the biogenic minerals and organic compounds which accumulate in lake sediments (Wetzel 2001). In particular, this relates to short term changes in biological activity, leading to seasonal patterns which can have important implications for interpreting environmental change from biological remains in lake sediments (Sorvari *et al.* 2002; Siver and Hamer 1992; Catalan *et al.* 2002; Koster and Pienitz 2006; Hausmann and Pienitz 2006). However, it is also important to consider the effects of seasonality on oxygen isotope records in palaeolimnology (Leng and Marshall 2004). Short term changes in the production of biogenic minerals and organic compounds, from which oxygen isotope ratios are measured, affect the seasonal weighting of lake sediments – i.e. the degree to which the sedimentary

isotope signal is biased towards a specific season. The specific aims of this chapter are to:

A Investigate the extent of seasonal variability in diatom standing crop at Lochnagar, in order to evaluate the effect of seasonal diatom production on oxygen isotope ratios of sedimentary diatom silica (further discussion of isotope fractionation and sediment accumulation is given in Chapter 7).

B Investigate the degree to which the taxonomic composition of the diatom community at Lochnagar varies with season and the potential for interpreting changes in the seasonal distribution of diatom production from sedimentary records.

6.1.2 Previous research

Seasonal studies have been carried out on the production of sediment components which carry isotope signatures of past lake water conditions, such as fine grained authigenic calcites (Leng and Marshall 2004) and ostracods (von Grafenstein *et al.* 1999; Keatings *et al.* 2002). Short term patterns in diatom crop size and productivity have been researched in great detail, revealing marked seasonal variability and contrasting patterns between sites (Hutchinson 1944; Lund 1954; 1963; Round 1960; Bailey-Watts 1978; Sommer and Stabel 1983; Sommer 1985; Reynolds 2006). The effects of seasonal patterns on the oxygen

isotope ratios of sedimenting planktonic diatoms ($\delta^{18}O_{silica}$) were studied at Lake Holzmaar, Germany (Raubitschek *et al.* 1999; Moschen *et al.* 2005; 2006). Raubitschek *et al.* (1999) conclude that the $\delta^{18}O_{silica}$ record is weighted towards spring and autumn lake conditions. However, given the variability in seasonal patterns observed for diatoms at different locations (e.g. King *et al.* 2002a), it is important to understand the site-specific patterns in seasonal diatom crop size in order to make reliable palaeoclimate interpretation from lake sediments.

The majority of research on seasonal patterns in diatom standing crop and production has focused on a) low elevation, eutrophic lakes; and b) lake phytoplankton (Hutchinson 1944; Lund 1965; Sommer 1986; Neale *et al.* 1991; Kilham *et al.* 1996). Studies into diatom seasonality of more remote, upland lakes are few (e.g. Felip *et al.* 1999; Fott *et al.* 1999; Pugnetti and Bettinetti 1999; Lotter and Bigler 2000; Brettum and Halvorsen 2004) and those which address seasonal changes in the periphyton of such lakes are even fewer (Jones and Flower 1986; King *et al.* 2002a) despite this being a major habitat for diatoms in remote oligotrophic lakes such as Lochnagar (Flower *et al.* 2007). Studies into the seasonal changes in periphytic diatom production have demonstrated similarities with phytoplankton – with marked productive periods in spring and autumn corresponding with nutrient and light availability (Round 1960; Hudon and Bourget 1981; Hoagland 1983; Roos 1983). It has been suggested (Round 1960; King *et al.* 2002a) that the seasonal range of periphytic diatom productivity increases with increased trophic state, due to greater nutrient availability during

peak growth periods (Round 1960; King *et al.* 2002a). Therefore, an oligotrophic lake such as Lochnagar might be expected to experience a weaker seasonal pattern in diatom crop size, or no pattern at all (King *et al.* 2002a).

Seasonal changes in the floristic composition of diatom assemblages are important to interpreting sedimentary $\delta^{18}O_{silica}$ records, especially if different taxa are associated with specific seasonal preferences. If certain taxa can be ascribed to particular seasons, it may be possible to infer changes in the extent of signal weighting according to certain seasons from the sediment record (Raubitschek *et al.* 1999). Some studies have revealed definite seasonal succession in the taxonomic composition of periphytic diatoms in oligotrophic and upland lakes (King *et al.* 2002a; Hausmann and Pienitz 2006; Koster and Pienitz 2006). However, it is important to consider the significance of temporal effects over the usually marked spatial heterogeneity within benthic communities (Jones and Flower 1986; King *et al.* 2002a; 2002b). For example, Jones and Flower (1986), through a study of epilithic and epipsammic communities in the littoral of the Round Loch of Glenhead, Scotland, observed spatial variability in diatom species composition of a degree equivalent to changes over the annual cycle.

The seasonal changes in phytoplankton assemblages at Lochnagar were analysed by Evzen Stuchlik between 1996-1998 (Flower *et al.* 2007; Figure 6.1). The taxonomic composition and low biomass of phytoplanktonic algae are typical

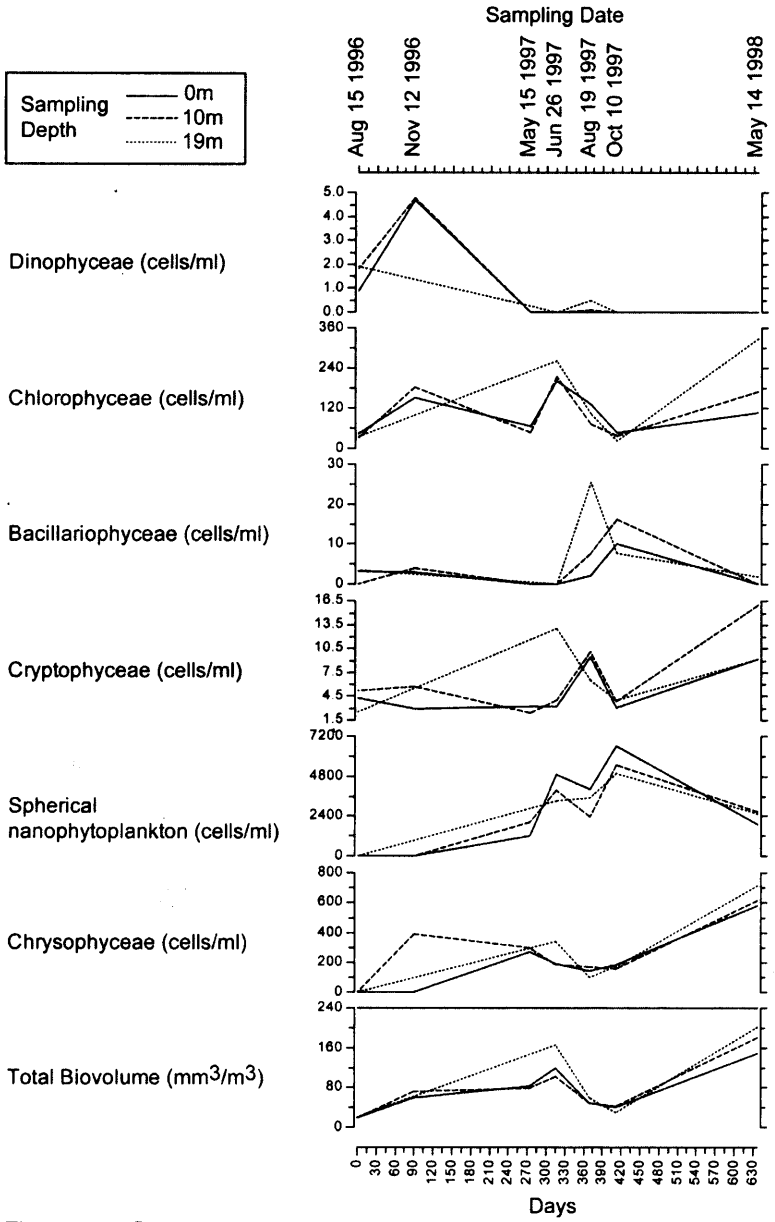

Figure 6.1: Seasonal patterns of phytoplankton in Lochnagar, August 1996 - May 1998 (Flower *et al.* 2007).

for oligotrophic, high elevation lakes in Europe and North America (Felip *et al.* 1999; Fott *et al.* 1999; Pugnetti and Bettinetti 1999; Brettum and Halvorsen 2004; Hausmann and Pienitz 2006). Planktonic diatoms in the form of *Aulacoseira* species were present in low concentrations in the water column from late

summer/early Autumn, following an inoculation phase in the deep waters during summer (Flower *et al.* 2007). The most common planktonic diatom, *Aulacoseira distans* var. *nivalis*, however, is more abundant in epilithon samples and could be described as tychoplanktonic – inhabiting both pelagic and benthic environments. Within surface sediments and sediment trap samples collected over the past 15 years by the Acid Waters Monitoring Network (AWMN) epilithic and epiphytic diatom taxa account for the overwhelming majority of all diatoms observed (D. Monteith pers. comm.; Flower *et al.* 2007). Figure 6.2 illustrates a typical littoral cross section from Lochnagar. Within the lake photic zone (to a depth ~ 8 m), large boulders and cobbles represent the primary habitat for diatom colonisation. Submerged aquatic macrophytes (providing habitats for epiphytic diatoms) and sedimentary environments (epipelon) account for a minority of potential habitats. Therefore, diatom growth at Lochnagar occurs primarily in the littoral benthos, specifically within the epilithon (Flower *et al.* 2007).

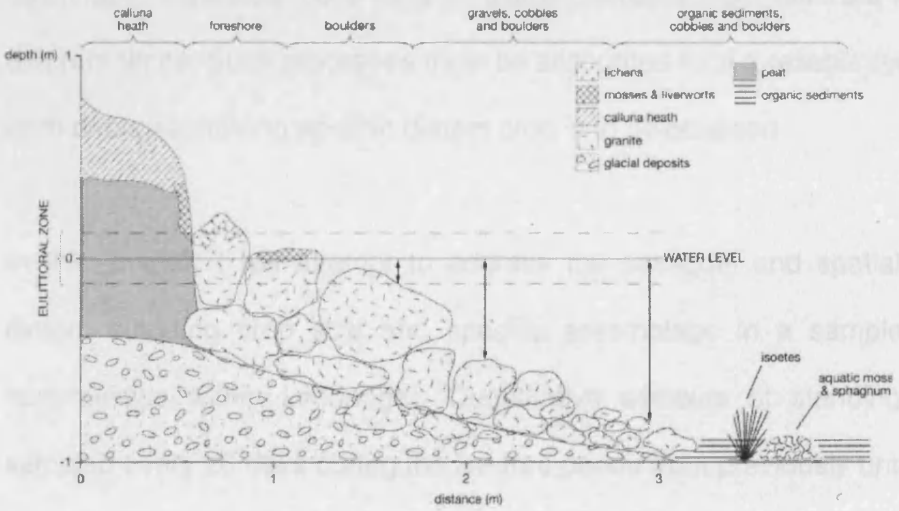

Figure 6.2: Cross section of the littoral habitat in Lochnagar (Flower et al. 2007).

One major difficulty in studying seasonal patterns in the production of epilithic diatom communities, compared to that of phytoplankton, is the irregularity in removal of dead cells from the substrate (Owen *et al.* 1979). In general, when sampling phytoplankton communities, it can be assumed that the cells suspended in the pelagic zone are currently, or have recently been, photosynthetically active and alive. Towards the end of the life cycle of a planktonic diatom, the cell settles out of the water column and is quickly removed from the sampling site (Round 1973). In contrast, epilithic diatoms remain *in situ* following death, until external forces such as grazing animals or hydraulic 'sloughing' removes them (Round 1973). Living epilithic communities live amongst the dead and decaying remains of their predecessors, and as a result, a biomass sample from a rock surface does not necessarily equate to the recent living community. In addition, a rock surface and its adhesive biofilm coating is an ideal trap for deposition of transported sediment from within the lake and catchment, invariably consisting of diatom remains from different habitats and different times. Such processes must be accounted for if a reliable record of short term changes in living epilithic diatom crop is to be obtained.

In this chapter I will attempt to address the seasonal and spatial patterns in diatom standing crop size and species assemblage in a sample of epilithic communities within Lochnagar. Quantitative samples of standing crop were sampled every 28 days during the ice-free period from previously untouched rock surfaces (old growth) (Chapter 3, Section 3.1.4). In addition, natural rock

surfaces were scrubbed clean and the 'new growth' which colonised the surface during the 28 day interval was sampled (Chapter 3, Section 3.1.4). Monthly observations over two years were combined to formulate a hypothetical sequence of epilithic diatom seasonal abundance to be used to examine the effects of seasonal patterns in diatom production on sedimentary $\delta^{18}O_{silica}$ records (Chapter 7).

6.2 Data sources and data analysis methods

Major ion and nutrient chemistry were routinely analysed as part of the Acid Waters Monitoring Network by the Fisheries Research Services (FRS) Freshwater Laboratory, Pitlochry and the Macaulay Land Use Research Institute, Aberdeen (Chapter 3, Table 6.1). All chemistry data presented in this chapter are those analysed by the Pitlochry laboratory, following the approach taken by the Acid Waters Monitoring Network publications (D. Monteith, pers. comm.). The Pitlochry bi-weekly silica (SiO_2) data, however, exhibit unusual step-like changes throughout the time-series and therefore appear to be subject to moderate analytical error. The Macaulay SiO_2 data replicate the Pitlochry dataset closely, without the stepped pattern, and are therefore used. Nutrient concentrations are particularly important to the discussion concerning temporal changes in diatom standing crop at Lochnagar. Nitrate (NO_3-N) and phosphate (PO_4-P) fluctuated markedly throughout the monitoring period, whereas ammonium (NH_4) was rarely

detected above analytical error (see Section 6.3.5). Water samples were collected three times during the summer of 2005 and analysed for NO_3-N, PO_4-P and NH_4 by S. Maberly at the Centre for Environmental Hydrology (CEH), Lancaster. Those analyses replicate well the data collected by the Pitlochry laboratory (C. Curtis, pers. comm.), including the marked variability in PO_4-P observed during 2005 (this chapter, Section 6.3.5). This suggests that the nutrient data used in this study are reasonably accurate, despite the low concentrations in Lochnagar.

The taxonomic composition of epilithic diatoms can vary markedly within the littoral of Lochnagar (Flower *et al.* 2007; Figure 6.3). In order to attempt to account for the spatial variability in diatom assemblages, three sites along the lake shoreline were sampled when possible, with three replicate samples at each site (Chapter 3, Section 3.1.4). In order to compare the extent of temporal and spatial variability in diatom assemblages, Detrended Correspondence Analysis (DCA) (Hill and Gauch 1980; Oksanen and Minchin 1997) was carried out for all samples using the VEGAN package in the statistical software R (Oksanen *et al.* 2006).

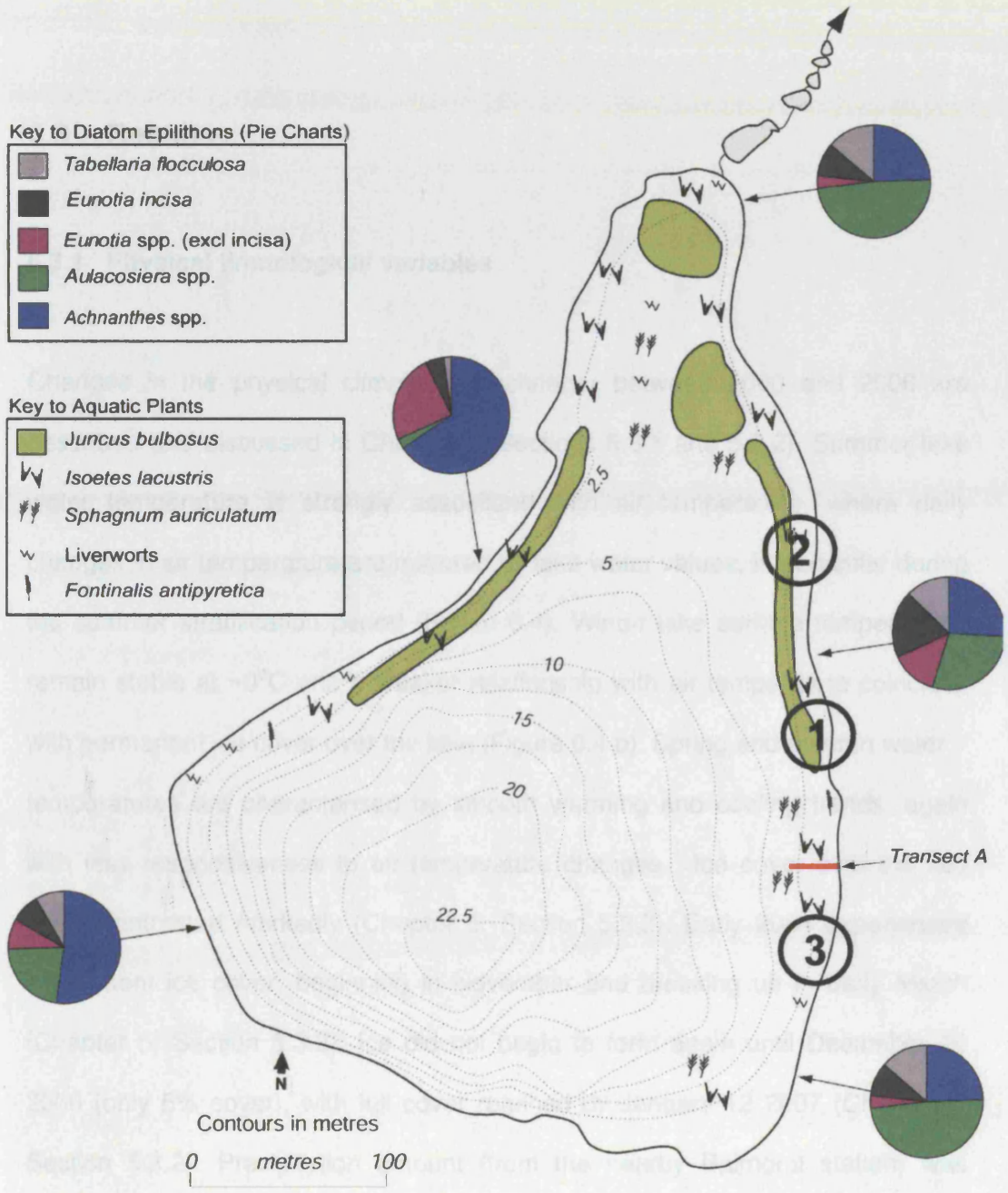

Figure 6.3: Spatial variability of diatom genera relative abundance, plus aquatic macrophytes. (modified from Flower *et al.* 2007). Circled numbers indicate the regular sampling sites for epilithic diatoms. Transect A = cross section in Figure 6.2.

6.3 Results

6.3.1 Physical limnological variables

Changes in the physical climate at Lochnagar between 2000 and 2006 are described and discussed in Chapter 5 (Sections 5.3.1 and 5.3.2). Summer lake water temperature is strongly associated with air temperature, where daily changes in air temperature are mirrored by lake water values, in particular during the summer stratification period (Figure 6.4). Winter lake surface temperatures remain stable at ~0°C and a weaker relationship with air temperature coincides with permanent ice cover over the lake (Figure 6.4 b). Spring and autumn water temperatures are characterised by smooth warming and cooling trends, again with less responsiveness to air temperature changes. Ice cover over the two years contrasted markedly (Chapter 5, Section 5.3.2). Early 2004 experienced intermittent ice cover, beginning in November and breaking up in early March (Chapter 5, Section 5.3.2). Ice did not begin to form again until December 26 2006 (only 5% cover), with full cover reached by January 12 2007 (Chapter 5, Section 5.3.2). Precipitation amount (from the nearby Balmoral station) was characterised by intermittent periods of heavy rainfall with no notable seasonal trend (Chapter 5, Section 5.3.1).

The thermal profile of Lochnagar is not available for 2004 and 2005, the period of diatom sampling, due to the unfortunate loss of the thermistor chain. Over the

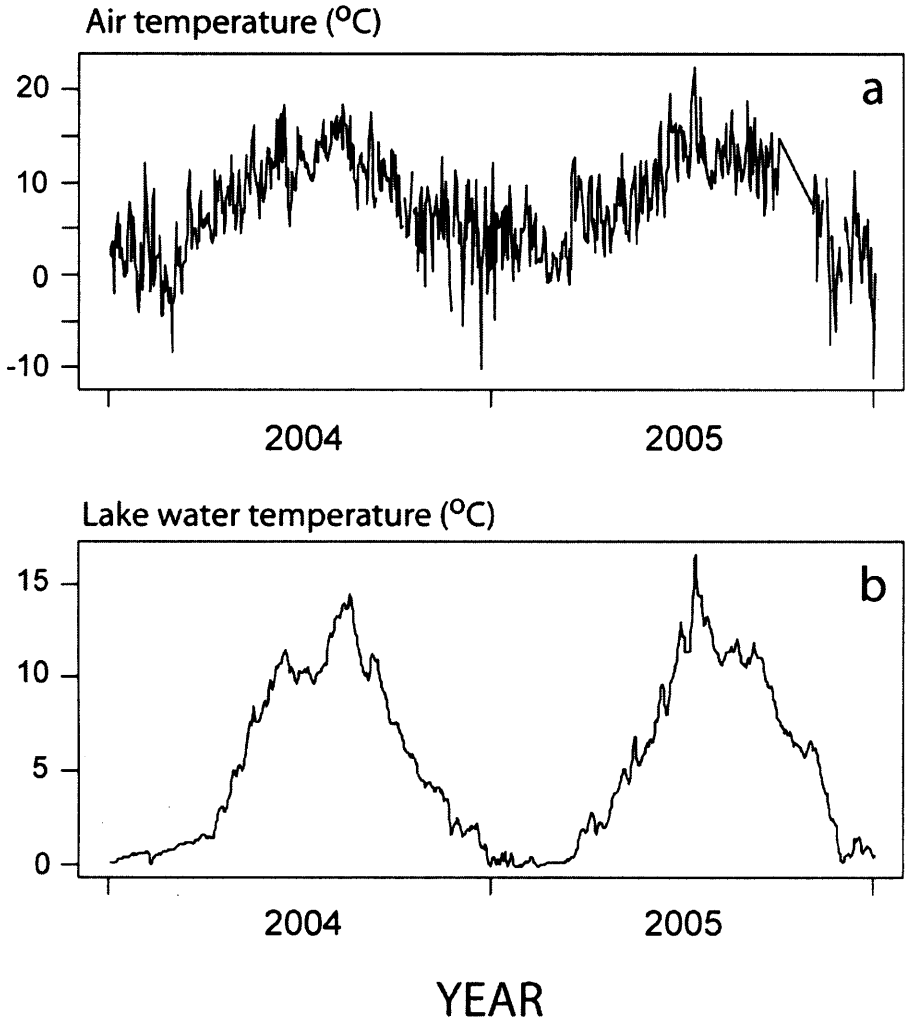

Figure 6.4: Air and water temperature (at 0.5 m deep) over two years at Lochnagar.

previous five years (detailed in Chapter 5, Section 5.3.2), lake overturn typically occurred following the break up of ice cover in the spring. Summer periods were characterised by periods of lake stratification prior to a second phase of overturn in the autumn. Winter ice cover usually coincided with a period of inverse stratification, whereby epilimnetic waters are cooled with respect to those in the hypolimnion (Chapter 5, Section 5.3.2).

Solar irradiance was monitored intermittently at Lochnagar between 12 April 2003 – 26 November 2003 and 15 June 2004 – 19 July 2004, with gaps in the dataset due to power failure to the automatic weather station (AWS). Over that period, despite marked short term variability, solar irradiance values followed a predictable pattern, with maximum values (upto ~ 0.6 kW/m^2.h) occurring in the summer months, declining sharply towards the winter (Figure 6.5), accentuated by shading by the high corrie wall (Chapter 2, Section 2.2.2; Hughes 2007).

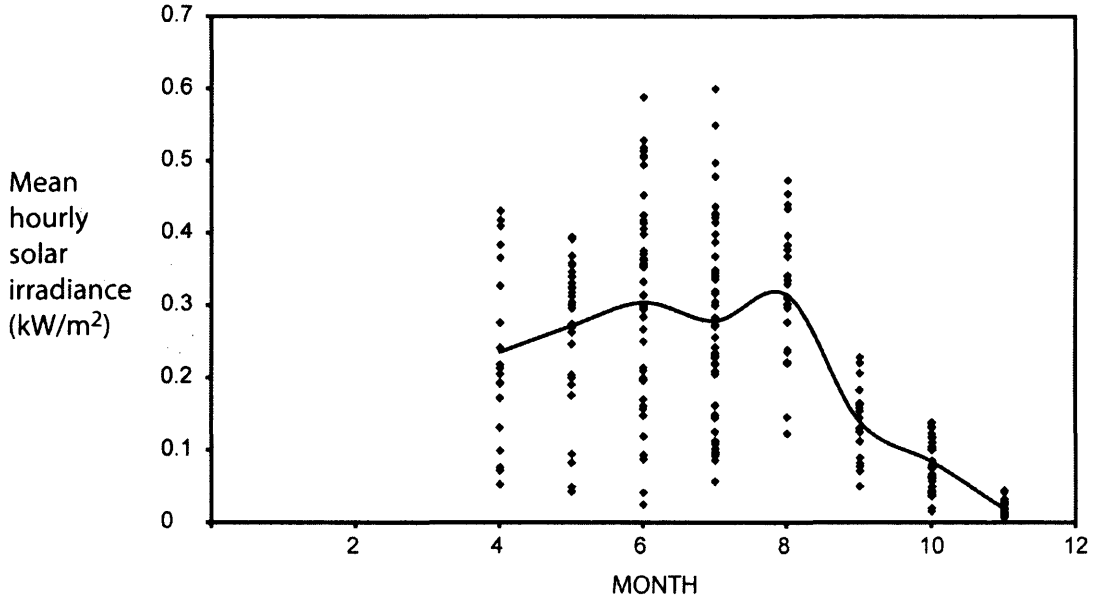

Figure 6.5: Solar irradiance at the Lochnagar automatic weather station against month for intermittent measurements made over 2003 and 2004. Points = daily means of hourly irradiance, solid line = monthly mean of hourly irradiance. Values based on half-hourly measurements.

6.3.2 Water chemistry: pH, conductivity and major ions

Changes in the concentration of major ions over two decades of monitoring at Lochnagar have been described in detail by Jenkins *et al.* (2007). The water chemistry of the lake was severely impacted by historically high levels of oxides

of sulphur and oxides and reduced forms of nitrogen deposited from the atmosphere (Jenkins *et al.* 2001; 2007; Montieth *et al.* 2007). However, the current chemistry status has substantially improved since the 1980s, most notably with a decline in anthropogenic sulphate causing an increase in pH (Jenkins *et al.* 2007; Monteith *et al.* 2007).

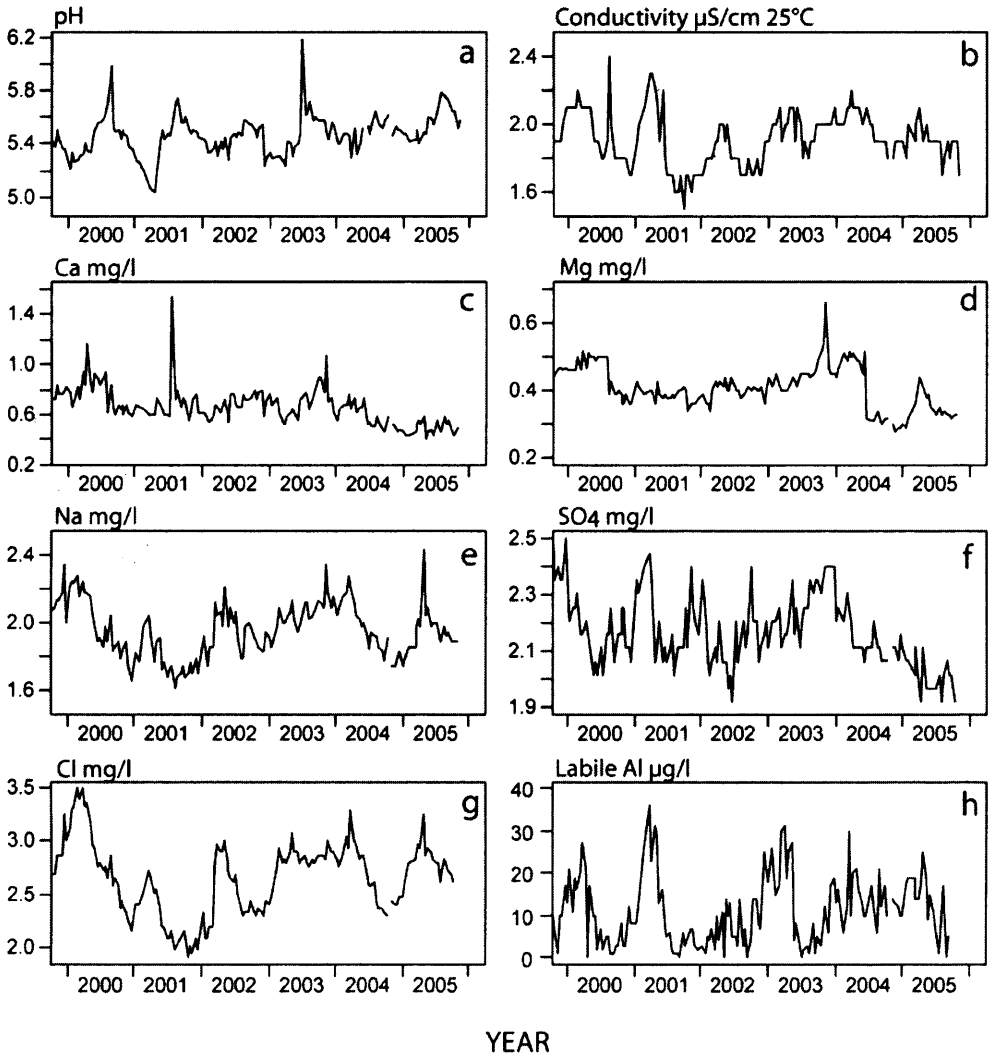

Figure 6.6: Lake water pH, conductivity and major ions in Lochnagar (2000-2005). Data supplied by FRS Pitlochry, collected through the Acid Waters Monitoring Network (AWMN).

Bi-weekly changes in pH, conductivity and major ions showed marked seasonal and inter-annual variability over 2000 - 2005 (Figure 6.6). pH increased slightly over the five years, with minimum values (~ 5.2) occurring during the winter months, and peak values (> 6) in the summer (Figure 6.6 a). By contrast, conductivity peaked during the spring of each year (~ 2.2 µS/cm), with minimum values (1.6 µS/cm) during the autumn (Figure 6.6 b). Ca and Mg declined slightly over the five years, with less marked seasonal fluctuations (Figure 6.6 c and d). However, Na, SO_4 and Cl exhibited marked variability between years, each peaking in early 2000, 2002 and 2004 with low values in late 2000, 2001 and 2004 (Figure 6.6 e, f and g), probably reflecting short term changes in the chemical composition of precipitation and runoff (Jenkins *et al.* 2007). Labile Al demonstrated the most marked short term variability over 2000 - 2005, with notable peaks (~ 30 µg/l) in early 2000, 2001 and 2003 and low values (~ 3 µg/l) in late 2000 and 2001 (Figure 6.6 h).

6.3.3 Water chemistry: nutrients

The nutrients PO_4-P, NO_3-N and SiO_2 fluctuated notably over intra- and inter-annual timescales over 2000 -2005, largely associated with changes in lake physical conditions (Figure 6.7). Throughout the majority of the monitoring record, PO_4-P values were below analytical detection limit, with short-lived periods of PO_4-P increases, usually not persisting for consecutive samples (Figure 6.7 c). P was detected in lake water in the spring of 2001, 2002 and

2003, shortly after the break-up of ice on the lake (Figure 6.7 a), at times of both lake mixing (TI ~ 0) and stratification (TI > 1) (Figure 6.7 b). During 2004, PO_4-P occurred during the late summer/autumn period, probably at the end of the summer stratification and the onset of autumnal overturn. During 2005, relatively high values of PO_4-P were measured during the summer (Figure 6.7 c). No thermal stratification data are available for this period, however the points appear to coincide with artificial fertilization of the catchment by the Cairngorms National Park Authority.

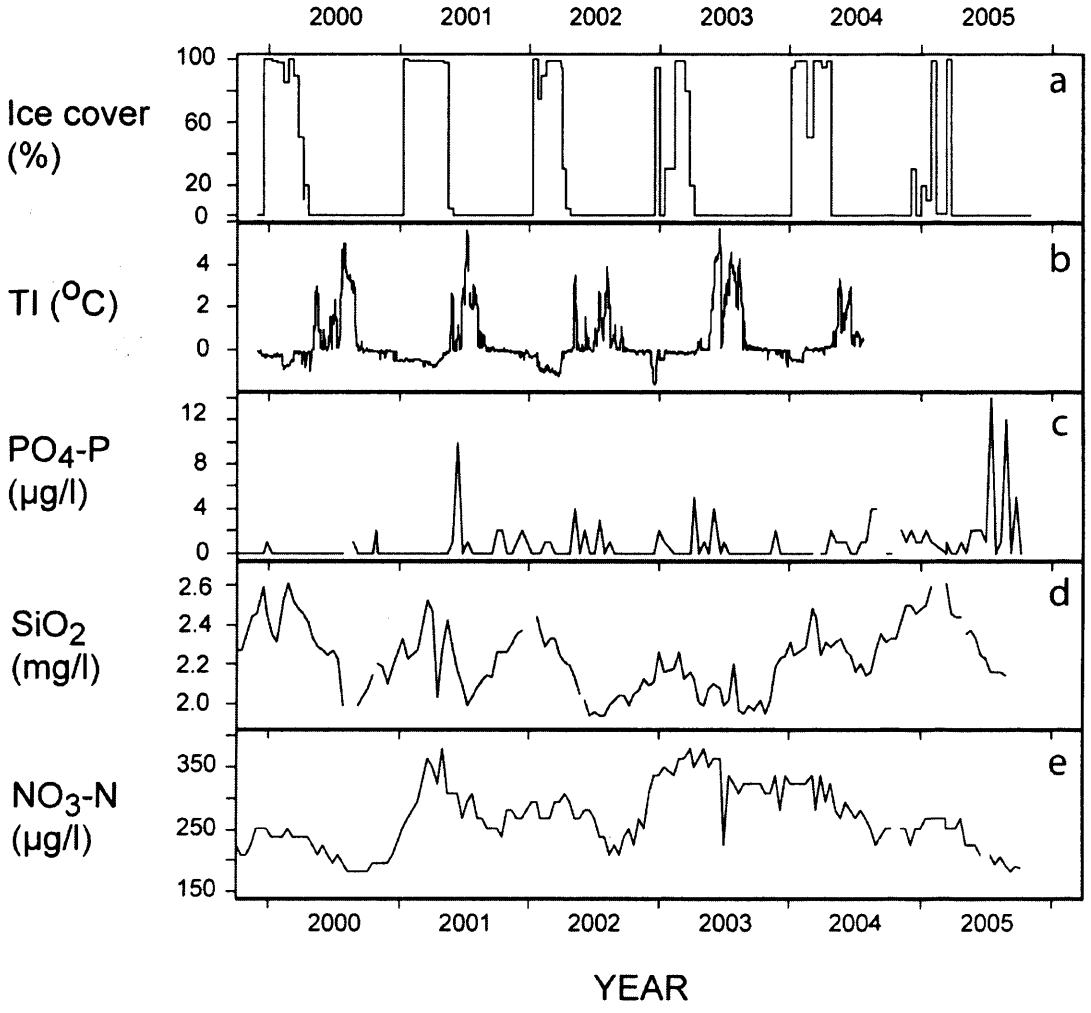

Figure 6.7: Nutrient chemistry at Lochnagar and its relation with physical lake conditions.

SiO_2 fluctuated markedly over the monitored period, with maximum values occurring during winter ice (~ 2.6 mg/l) and periods of rapid decline following ice-out (Figure 6.7 d). SiO_2 minima (~ 2 mg/l) occurred repeatedly during late summer (Figure 6.7 d). The seasonal cycle was most marked during 2000, 2001, 2002 and 2005, whereas 2003 and 2004 experienced less marked changes, with notably low winter maxima preceding 2003 and limited SiO_2 depletion during both 2003 and 2004 (Figure 6.7 d).

NO_3-N followed a repetitive pattern similar to SiO_2, however very few traces of NH_4^+ were detected. NO_3-N maxima occurred during the winter periods of each year, during the period of ice cover, with notable peaks in early 2001 and 2003 (~ 350 µg/l) and minima during late 2000 and 2005 (~ 200 µg/l) (Figure 6.7 e). NO_3-N followed a fairly repetitive pattern of declining levels throughout the ice-free period of each year, however the decline was less marked during 2003, coinciding with pronounced lake water stratification during the summer (Figure 6.7 b).

6.3.4 Nutrient ratios

Molar ratios of Si:N, Si:P and N:P were calculated for the five years of nutrient chemistry monitoring in order to infer changes in potential nutrient limitation to primary productivity (Figure 6.8). Si:N ratios, using both NO_3-N and total N (TN) values fluctuated around 2, and were consistently greater than the Redfield ratio

(1), except for a single value analysed in May 2005, where Si/N was 0.7 (Figure 6.8 a). Si:P fluctuated between ~ 40 and ~ 550, using total phosphorus (TP) values, with one exceptionally high value of 1114 during July 2005 (Figure 6.8 b). Where PO_4-P values are used, Si:P values were consistently higher, often >1000 (Figure 6.8 b). The ratios of soluble (NO_3-N:PO_4-P) and total (TN:TP) nitrogen and phosphorus fluctuated stochastically throughout the five monitored years (Figure 6.8 c). Soluble N:P reached a maximum (836) in early 2003 and a minimum (33) during July 2005 (Figure 6.8 c). Total N:P reached a maximum of 559 in July 2005, and minima of <30 during most years (Figure 6.8 c).

6.3.5 Diatom cell density

6.3.5.1 Cross-calibration of microscope techniques

Figure 6.9 compares % relative abundance estimates for the four major genera in the epilithon of Lochnagar using an inverted microscope with 400 x magnification and a standard microscope using fixed slides and immersion oil at 1000 x magnification. Only estimates for *Tabellaria* are reliably comparable between methods (Figure 6.9 d). *Achnanthes* estimates are consistently higher under 1000x magnification than those estimated using inverted microscopy at 400x magnification (Figure 6.9 a), whereas *Eunotia* estimates are consistently lower at 1000x (Figure 6.9 c). *Aulacoseira* estimates are more randomly distributed, however the general pattern is less biased towards over estimation using a

particular method (Figure 6.9 b). Use of high powered (1000x) magnification, fixed microscope slides and oil immersion is a more accurate method in terms of taxonomy and reliable assessment of relative abundance. The 1000x

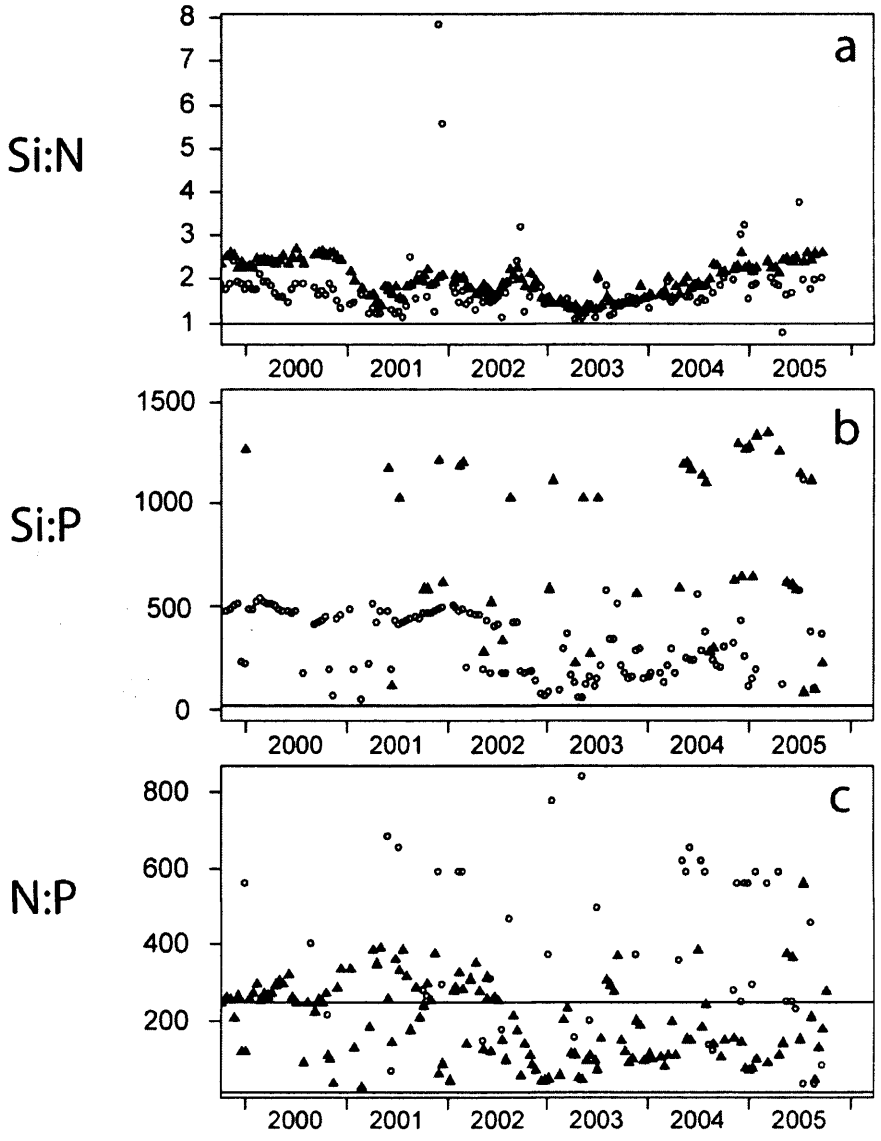

Figure 6.8: Molar ratios of major nutrients in Lochnagar water over time, (a) silicon vs. nitrogen; (b) silicon vs. phosphorus; (c) nitrogen vs. phosphorus. Filled triangles represent ratios of soluble reactive concentrations (i.e. PO_4-P and NO_3-N), open circles represent ratios of total molar concentrations (i.e. total nitrogen and phosphorus). Horizontal lines represent likely limiting values, whereby points below the line in (a) and (b) indicate silicon limitation, points above the upper line in (c) indicate phosphorus limitation, points between the lines in (c) indicate co-limitation by nitrogen and phosphorus and points below the bottom line in (c) indicate nitrogen limitation.

methodology, however, does not readily enable assessment of the relative contribution of live and dead cells – identified according to the presence/absence of chloroplasts within the cell contents. The use of an inverted microscope and Utermohl chamber (Wetzel and Likens 2000) is a more reliable method for analysis of 'fresh' material (i.e. with no chemical pretreatment). The inverted microscope is also beneficial in determining total cell density – allowing a greater amount of flexibility than fixed slide methods, since the volume of material analysed can be altered according to the density of cells in that particular sample. However, the weaker magnification (400x) associated with the inverted microscope inevitably leads to taxonomic errors. In this case, it is evident that small *Achnanthes* cells have been mis-identified as *Eunotia* using the inverted microscope technique, due to their similar small dimensions and appearance in girdle view. This has led to an overestimation of *Eunotia* relative abundance at 400x and a corresponding underestimation of *Achnanthes*. The difference in *Aulacoseira* counts under the two methods is probably due to the random distribution, or otherwise, of *Aulacoseira* cells within the samples. Since each sample analysed is a sub-sample of a greater population, it is necessary for the cells within a subsample to be randomly distributed if accurate estimates of the total population are to be obtained. *Aulacoseira* grow in lakes in large chain colonies, with cells firmly fixed together by organic bonds and spines. The chemical and physical pretreatments carried out in the preparation of fixed slides for high powered microscopy has the effect of destroying these bonds, and disaggregating diatom colonies, such that the diatom frustules are well mixed

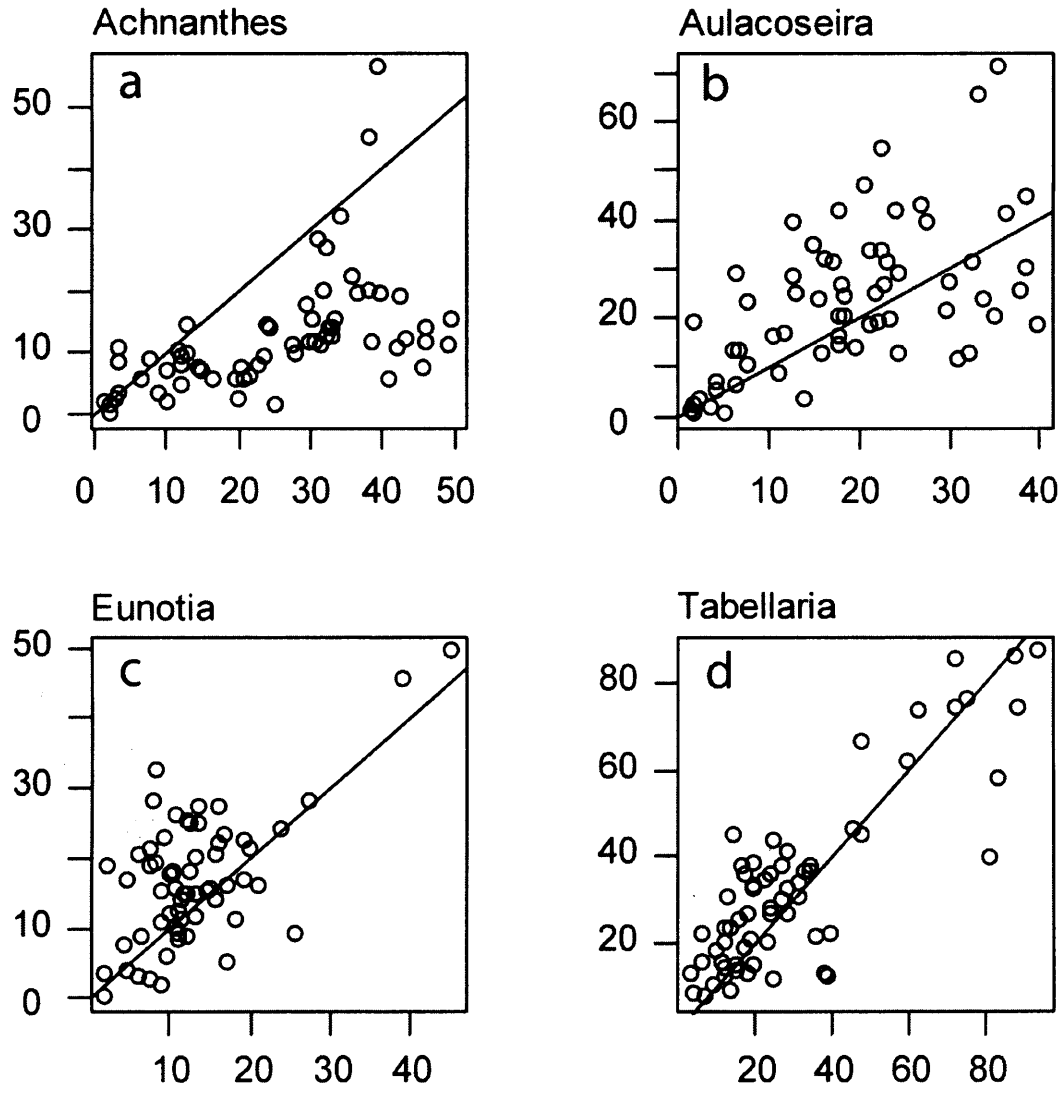

Figure 6.9: Comparison between % relative abundance of four major genera as counted using inverted (y axes) and high power microscope (x axes).

when analysed under a microscope.. However, vigorous shaking in the pretreatment prior to inverted microscope analysis does not effectively break up *Aulacoseira* colonies. This has the effect of reducing the randomness within the sample, such that observation of a single *Aulacoseira* cell is likely to coincide

with observation of multiple cells, and likewise absence of observation of any cells is more likely. *Tabellaria* also form chain colonies in nature, however the bonds between cells are weaker than those of *Aulacoseira* and it was rare to observe an intact *Tabellaria* colony using the inverted microscope. *Tabellaria* cells are also extremely distinctive using both methods, in both girdle and valve view. As a consequence, the % relative abundance of *Tabellaria* is reasonably consistent between methods. This consistency in *Tabellaria* abundance is important, since it indicates that despite certain taxonomic errors using 400x magnification, the total population of diatom frustules counted was the same for both methods, and consequently there is no evidence for systematic exclusion of particular taxa (i.e. those with very small frustules) using the inverted microscope. Consequently, estimates of total cell density derived from inverted microscope counts can be reliably assumed to relate to the same assemblage analysed in more detail at higher magnification.

6.3.5.2 Comparison between live and dead cells

One difficulty in tracking seasonal patterns in benthic communities is the potential presence of old diatom frustules which did not grow in the environment in which they were sampled. Such old frustules may have been transported from other sites within the lake, be re-suspended from the sediments or persist *in situ* having grown at a previous time under different conditions. By comparing the diatom cell density from standing 'old' epilithic growth and 'new' growth upon rock

surfaces, cleaned 28 days prior to sampling, the relative influence of recent growth on the overall standing biomass can be partially assessed. In order to account for resuspended diatom frustules, the relative abundance of 'live' cells – i.e. those containing intact chloroplasts and other cell contents and 'dead' cells – i.e. those with no cell contents was enumerated.

Within 'new' growth samples, the density of live cells (cells/mm^2) greatly outweighs that of dead cells, especially for *Aulacoseira* and *Tabellaria* (Figure 6.10 b and d). The trends in live and dead cell density are generally similar throughout, except for *Achnanthes*, where an apparent lag takes place between peak density in live and dead cells (Figure 6.10). For 'old' growth (Figure 6.11), dead cells account for a greater proportion of the overall assemblage, however the similarity between the pattern of live and dead cells is also high, especially for *Achnanthes* and *Eunotia*, where the density of dead cells almost equals that of live cells (Figures 6.11 a and c). For both new and old growth, *Aulacoseira* and *Tabellaria* are dominated by live cells, however the similarity in temporal trend between live and dead cells remains (Figures 6.10 and 6.11).

The similarity between patterns of live and dead cell density for both new and old growth suggests that epilithic biofilms during the monitored period have a short turnover period between growth and removal from the substrate. Dead cells most likely originate primarily from recently living cells in situ. Had a significant proportion of the dead cells counted arrived via re-suspension of sedimentary

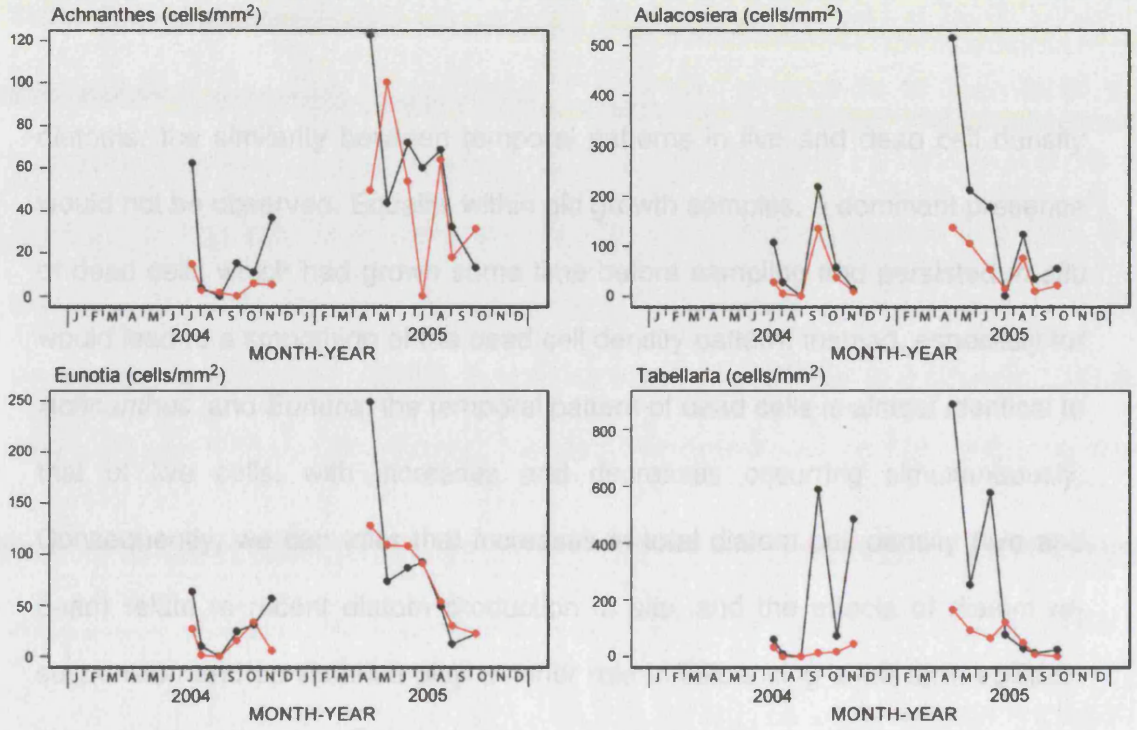

Figure 6.10: Comparison between live (black points and lines) and dead (red points and lines) cells for new growth.

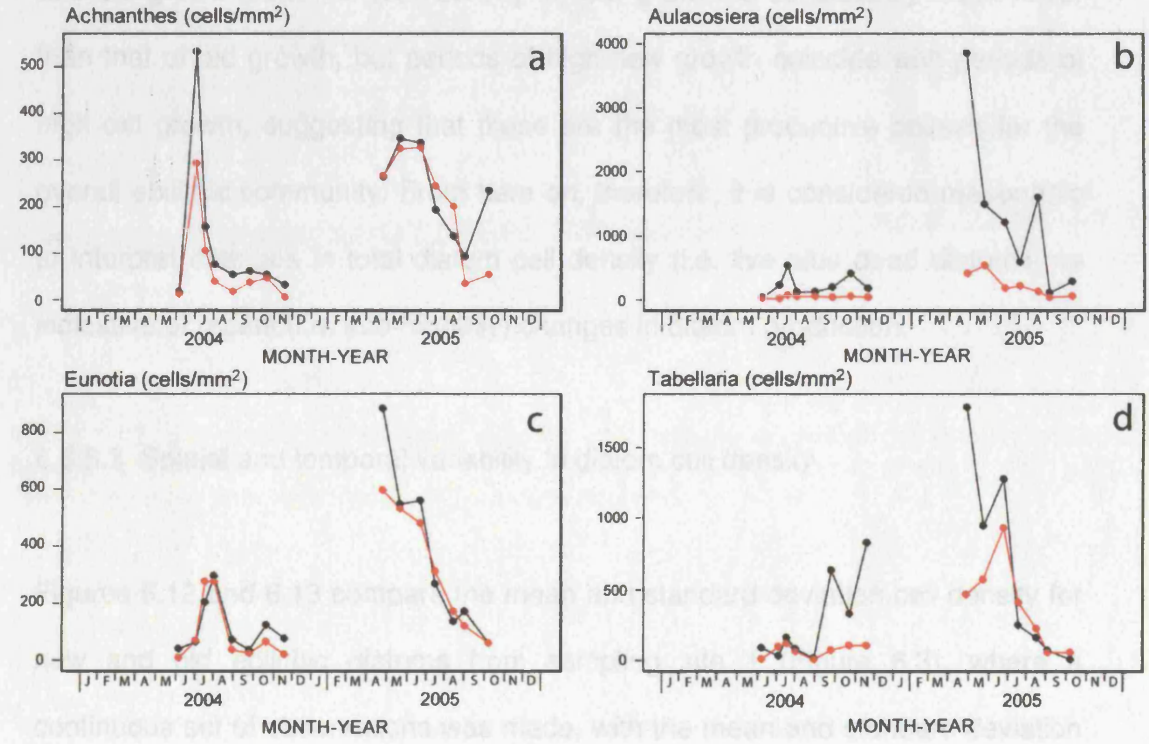

Figure 6.11: Comparison between live (black points and lines) and dead (red points and lines) cells for old growth.

diatoms, the similarity between temporal patterns in live and dead cell density would not be observed. Equally, within old growth samples, a dominant presence of dead cells which had grown some time before sampling and persisted *in situ* would lead to a smoothing of the dead cell density pattern. Instead, especially for *Achnanthes* and *Eunotia*, the temporal pattern of dead cells is almost identical to that of live cells, with increases and decreases occurring simultaneously. Consequently, we can infer that increases in total diatom cell density (live and dead) relate to recent diatom production *in situ*, and the effects of diatom re-suspension and persistence play a minor role in influencing short term epilithon biomass at Lochnagar. This is further supported by the similarity between new and old growth patterns. Cell density in new growth is consistently much lower than that of old growth, but periods of high new growth coincide with periods of high old growth, suggesting that these are the most productive phases for the overall epilithic community. From here on, therefore, it is considered reasonable to interpret changes in total diatom cell density (i.e. live plus dead diatoms) as indicative of recent (i.e. sub-monthly) changes in diatom production.

6.3.5.3 Spatial and temporal variability in diatom cell density

Figures 6.12 and 6.13 compare the mean and standard deviation cell density for new and old epilithic diatoms from sampling site 1 (Figure 6.3), where a continuous set of observations was made, with the mean and standard deviation for all sampling points across all three sampled sites, which due to logistical

constraints could not always be sampled. During the latter part of 2005, between-site standard deviation is generally of a similar magnitude to the within site standard deviation (i.e. that between replicate samples from an individual boulder), however during late 2004, between-site standard deviations range from less than half the within-site standard deviation (e.g. *Achnanthes* and *Eunotia*, old growth, September and October 2004) to almost equal (*Tabellaria*, old growth, October 2004) (Figure 6.13). In both cases, the standard deviations are high, equaling the

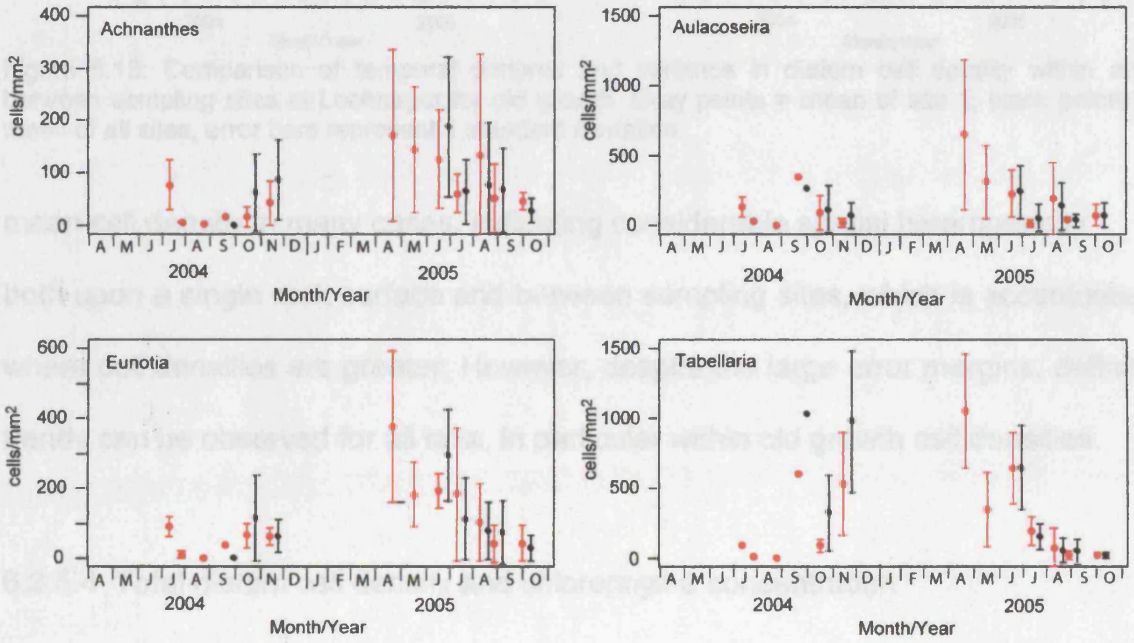

Figure 6.12: Comparison of temporal patterns and variance in diatom cell density within and between sampling sites at Lochnagar for new growth. Red points = mean of site 1, black points = mean of all sites, error bars represent 1 standard deviation.

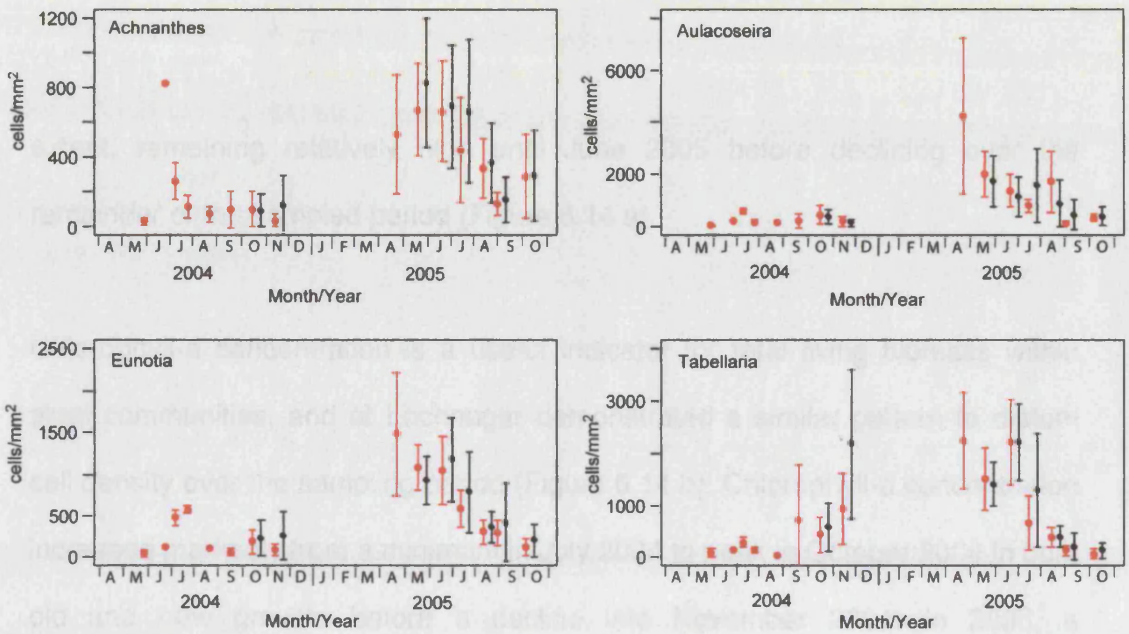

Figure 6.13: Comparison of temporal patterns and variance in diatom cell density within and between sampling sites at Lochnagar for old growth. Grey points = mean of site 1, black points = mean of all sites, error bars represent 1 standard deviation.

mean cell density in many cases, indicating considerable spatial heterogeneity both upon a single rock surface and between sampling sites, which is accentuated where cell densities are greater. However, despite the large error margins, definite trends can be observed for all taxa, in particular within old growth cell densities.

6.3.5.4 Total diatom cell density and chlorophyll-a concentration

Between May – October 2004, total cell densities (means of all samples) peaked in early June and again in October (Figure 6.14 a). The highest observed cell density occurred in March 2005, before a sharp decline over the remainder of the year. New growth diatom density also peaked in March 2005, to a less marked

extent, remaining relatively high until June 2005 before declining over the remainder of the sampled period (Figure 6.14 a).

Chlorophyll-a concentration is a useful indicator for total living biomass within algal communities, and at Lochnagar demonstrated a similar pattern to diatom cell density over the sampling period (Figure 6.14 b). Chlorophyll-a concentration increased markedly from a minimum in July 2004 to peak in October 2004 in both old and new growth, before a decline into November 2004. In 2005, a chlorophyll-a maximum in March was followed by a decline towards June (Figure 6.14 b). A further, slight increase in chlorophyll-a took place during August 2005 (Figure 6.14 b). Temporal patterns in chlorophyll-a were most similar to patterns in *Tabellaria* abundance rather than total diatom cell density, in particular with regards to peak values in both autumn 2004 and spring 2005 (Figures 6.11 d and 6.14 b).

6.3.5.5 Comparing diatom cell density with physical and chemical variables

Obtaining a continuous sequence of diatom abundance data throughout the monitoring period was considerably hindered by weather conditions (heavy snow and lake ice cover) preventing access and sampling at the site during the winter. Consequently, the size of the dataset is too small to make definite conclusions concerning the effects of physical and chemical variables on diatom standing crop size over time. Diatom cell density of both new and old growth reached a

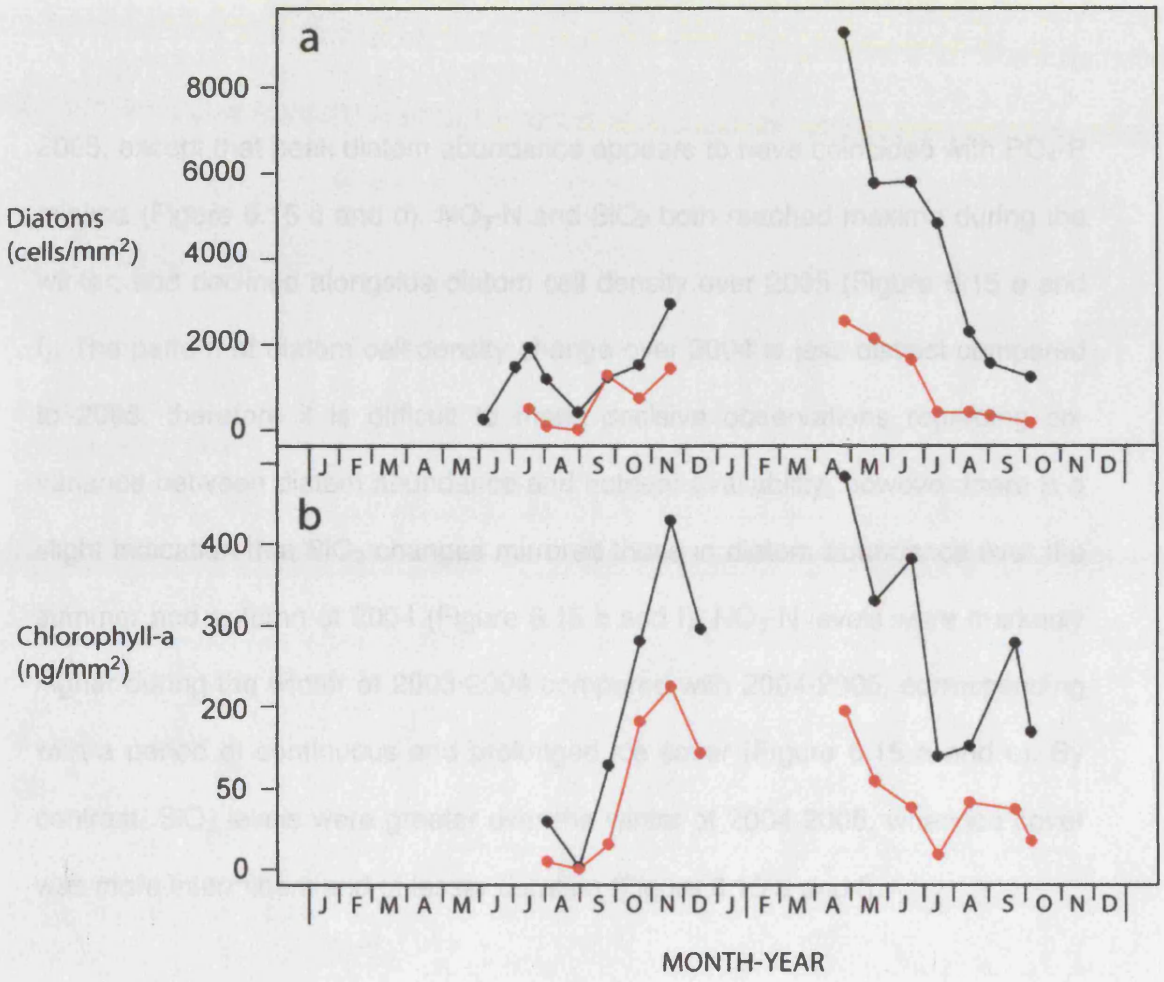

Figure 6.14: (a) Total diatom abundance and (b) Chlorophyll-a concentration in old (black lines) and new (red lines) epilithic biofilms.

maximum in March 2005, shortly after the final break up of an intermittent winter ice cover (Figure 6.15 and c). At the point of maximum cell density, water temperature was ~ 3°C (Figure 6.15 b) and light availability was probably low, both in terms of total irradiance and day length. At the point of spring ice-out and lake water overturn, PO_4-P is often detected in the waters of Lochnagar (Figure 6.7 c), however over 2004 and 2005, this was not the case, with PO_4 levels 'peaking' during the summer, especially in 2005 (Figure 6.15 d). There is no apparent co-variance between diatom cell density and PO_4 over 2004 and

2005, except that peak diatom abundance appears to have coincided with PO_4-P minima (Figure 6.15 c and d). NO_3-N and SiO_2 both reached maxima during the winter, and declined alongside diatom cell density over 2005 (Figure 6.15 e and f). The pattern of diatom cell density change over 2004 is less distinct compared to 2005, therefore it is difficult to make decisive observations regarding co-variance between diatom abundance and nutrient availability, however there is a slight indication that SiO_2 changes mirrored those in diatom abundance over the summer and autumn of 2004 (Figure 6.15 c and f). NO_3-N levels were markedly higher during the winter of 2003-2004 compared with 2004-2005, corresponding with a period of continuous and prolonged ice cover (Figure 6.15 a and e). By contrast, SiO_2 levels were greater over the winter of 2004-2005, when ice cover was more intermittent and of lesser duration (Figure 6.15 a and f).

6.3.5.6 Fitting a generalised pattern of seasonal diatom abundance

In order to investigate the effect of seasonal changes in diatom standing crop on the annual average oxygen isotope composition of sedimenting diatom silica (investigated in Chapter 7) a composite seasonal diatom abundance curve was formulated (Figure 6.16). Figure 6.16 attempts to summarise monthly diatom standing crop based on observed average cell density estimated during 2004 and 2005. Although there are some differences between years – especially concerning May and June diatom cell density, which was relatively low during 2004 and high during 2005, overall the data suggest a generalised pattern of

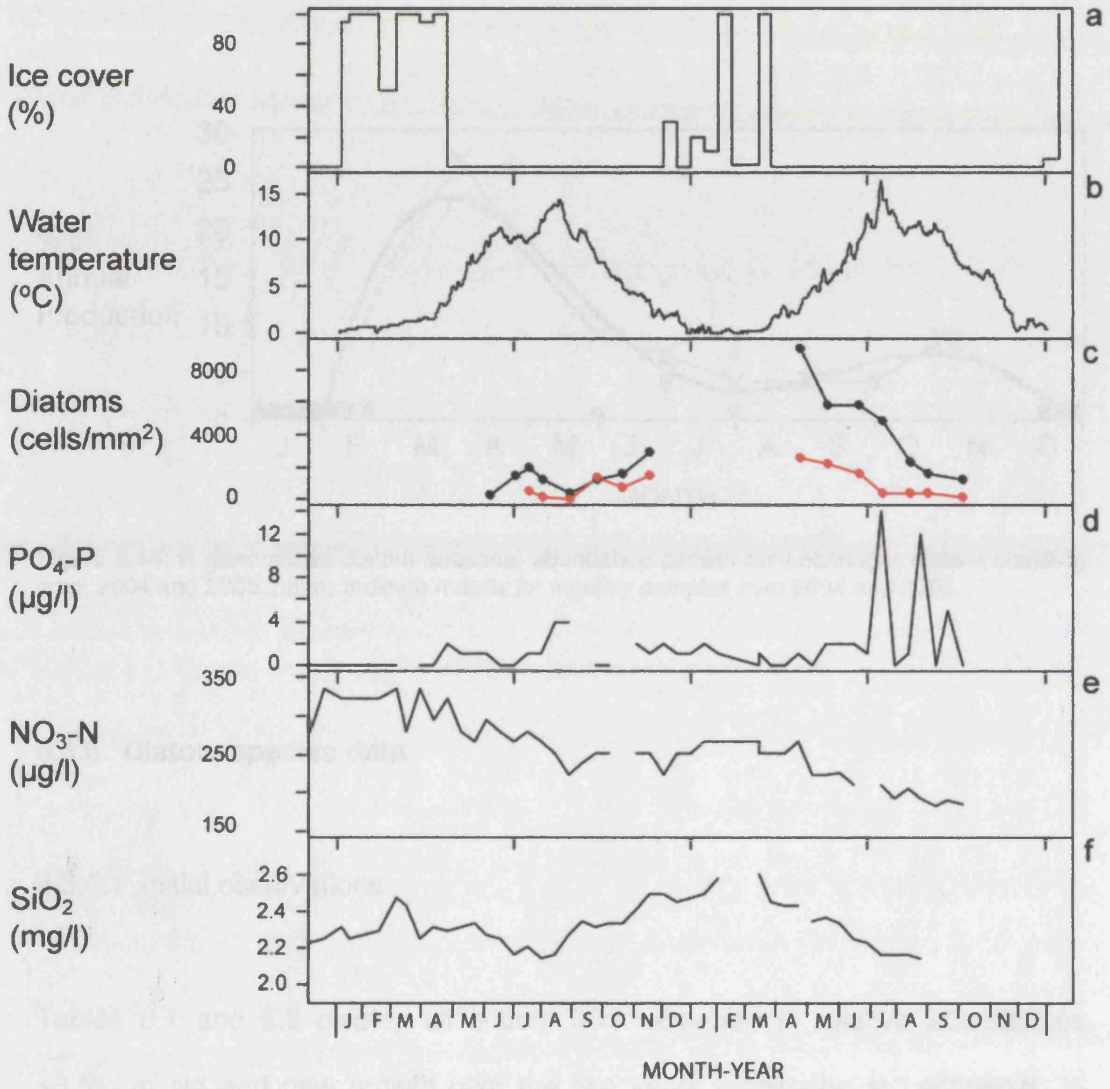

Figure 6.15: Detailed comparison diatom cell density, physical lake conditions and nutrient chemistry over 2 years.

high productivity during spring, shortly after ice melt, and a second, lesser phase of productivity during the autumn. A 6-point polynomial curve was fitted to the average cell density per month for the two years monitored, which implies that over 50% of the total annual production took place during March and April. Zero productivity is assumed during the ice-cover period.

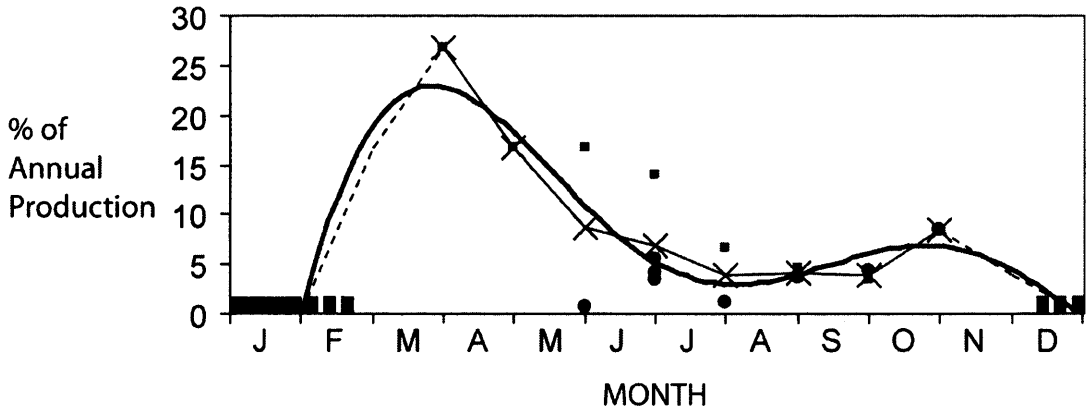

Figure 6.16: A generalised diatom seasonal abundance pattern for Lochnagar diatom standing crop, 2004 and 2005, points indicate means for monthly samples over 2004 and 2005.

6.3.6 Diatom species data

6.3.6.1 Initial observations

Tables 6.1 and 6.2 display all diatom taxa observed in relative abundances >0.5% in old and new growth over the two years monitoring at Lochnagar. In general, the most common taxa tend to occur frequently throughout the year, however many taxa have maximum abundances notably greater than their mean, indicating a degree of variability in relative abundance with time. For example, *Achnanthes helvetica* reached maximum abundance in May 2004 and *Staurosirella pinnata* reached maximum abundance in May 2005.

6.3.6.2 Between-site and between-sample heterogeneity

Figures 6.17 and 6.18 plot the results of Detrended Correspondence Analysis (DCA) of all individual diatom counts (Figures 6.17a and 6.18a) and average diatom relative abundance for each sampling site (Figures 6.17b and 18b) for old growth (Figure 6.17) and new growth (Figure 6.18). The size of the polygons, representative of samples taken on particular dates, is indicative of the diversity amongst samples. The degree of overlap between polygons indicates the similarity, or otherwise, of diatom assemblages identified between sampling dates. In both cases, it is evident that the variance between samples taken on an individual day is almost equivalent to that within the whole dataset, over all sampling visits (Figures 6.17a and 6.18a). The variability within samples taken on a particular date is predictably greater according to the number of samples taken. However, despite this there are distinct periods where the variability between species assemblages is notably less than others – for example, for new growth sampled on 10/20/04 (Figure 6.18a) the points are tightly grouped, whereas during June, July and September 2005 (15/06/05; 13/07/05 and 07/09/05) the points are highly scattered (Figure 6.18a). For old growth, the periods of greatest scatter are September 2004, June 2005 and August 2005, however samples from October 2004 are tightly clustered (Figure 6.17a). Temporal patterns are most notable in new growth – where there is an association between samples taken in September and October 2004; April and May 2005 and July-September 2005, despite considerable overlap with these associations (Figure 6.18a).

Table 6.1: All diatom taxa with maximum relative abundance > 0.5% in old growth for all sites sampled. Max % = maximum % abundance of a particular taxon within a sample; avg % = mean % abundance of that taxon; sd = standard deviation; date of max % = date of maximum occurrence of the particular taxon; frequency of occurrence = percentage of sampling dates where a particular taxon was recorded.

Code	Taxon	max %	avg %	sd	date of max %	frequency of occurrence (%)
AC013A	*Achnanthes minutissima*	1.3	0.07	0.21	23/08/2005	47
AC022A	*Achnanthes marginulata*	25.4	12.44	6.00	15/06/2005	100
AC042A	*Achnanthes detha*	1.1	0.03	0.17	13/07/2005	13
AC046A	*Achnanthes altaica*	2.4	0.09	0.38	22/05/2005	27
AC046B	*Achnanthes altaica* var. *minor*	5.1	0.76	0.98	15/06/2005	87
AC048A	*Achnanthes scotica*	7.3	0.19	0.88	07/09/2005	27
AC134A	*Achnanthes helvetica*	32.3	3.93	4.65	05/05/2004	100
AC134B	*Achnanthes helvetica* var. *alpina*	6.4	1.20	1.37	22/05/2005	87
AC134C	*Achnanthes helvetica* var. *minor*	14.2	2.30	2.27	15/06/2004	100
AC143A	*Achnanthes oblongella*	1.5	0.12	0.30	13/07/2005	47
AM001A	*Amphora* aff. *ovalis*	1.0	0.02	0.12	28/07/2004	13
AU005A	*Aulacosiera distans* var. *distans*	4.6	0.14	0.62	13/07/2005	27
AU005B	*Aulacosiera distans* var. *nivaloides*	14.1	0.92	1.98	25/08/2004	87
AU005E	*Aulacosiera distans* var. *nivalis*	39.6	14.87	8.69	07/09/2005	100
AU010A	*Aulacosiera perglabra*	8.7	0.20	1.05	07/09/2005	20
AU010B	*Aulacosiera perglabra* var. *florinae*	1.8	0.05	0.27	22/05/2005	13
AU028A	*Aulacosiera tenella*	4.2	0.62	1.03	15/06/2004	80
AU032A	*Aulacosiera lacustris*	5.5	0.83	1.03	23/08/2005	93
AU9972	*Aulacosiera distans* var. *seppentrionalis*	8.3	1.02	1.40	15/06/2005	93
BR006A	*Brachysira brebessonii*	9.6	1.23	2.03	23/08/2005	93
CM046A	*Encyonema borealis*	1.4	0.26	0.39	22/09/2004	87
DT021A	*Diatoma mesodon*	1.0	0.12	0.25	28/07/2004	53
EU002A	*Eunotia pectinalis*	0.8	0.10	0.20	23/08/2005	60
EU002D	*Eunotia pectinalis* var. *undulata*	1.0	0.05	0.18	15/06/2005	27
EU003A	*Eunotia praerupta*	0.9	0.05	0.16	05/05/2004	33
EU003B	*Eunotia praerupta* var. *bidens*	0.9	0.01	0.11	22/05/2005	7
EU009A	*Eunotia exigua*	4.3	0.30	0.61	22/09/2004	93
EU011A	*Eunotia rhomboidea*	3.3	0.09	0.43	23/08/2005	20
EU015A	*Eunotia denticulata*	7.3	1.06	1.42	23/08/2005	80
EU035A	*Eunotia major*	1.4	0.05	0.19	07/09/2005	27
EU040A	*Eunotia paludosa*	2.4	0.13	0.38	30/06/2004	53
EU047A	*Eunotia incisa*	15.4	5.20	3.21	07/09/2005	100
EU049B	*Eunotia curvata* var. *subarcuata*	2.8	0.39	0.66	22/09/2004	73
EU060A	*Eunotia pirla*	0.9	0.02	0.12	07/09/2005	7
EU105A	*Eunotia subarcuatoides*	38.2	5.01	6.54	30/06/2004	100
EU108A	*Eunotia intermedia*	7.5	0.10	0.87	02/06/2004	7
EU996A	*Eunotia aff arcus*	0.9	0.01	0.11	05/05/2004	7
EU997A	*Eunotia* sp.	2.9	0.19	0.49	23/08/2005	47
EU998A	*Eunotia nygaardii*	12.6	0.19	1.47	28/07/2004	27
EY003A	*Encyonema hebredica*	1.5	0.15	0.31	28/07/2004	80

EY014A	*Encyonema perpusilla*	1.8	0.19	0.34	23/08/2005	73
EY016A	*Encyonema silesiaca*	2.0	0.15	0.36	22/05/2005	40
EY998A	*Encyonema* sp.	0.9	0.01	0.11	05/05/2004	7
FR005Z	*Fragilaria virescens*	14.1	1.82	2.89	23/03/2005	73
FR007A	*Fragilaria voucheriae*	0.7	0.01	0.09	22/09/2004	13
FR009A	*Fragilaria capucina*	18.0	0.51	2.44	07/09/2005	47
FR064Z	*Fragilaria exigua*	3.8	0.21	0.61	15/06/2005	67
FU002B	*Frustulia rhombiodes* var. *saxonica*	6.6	0.83	1.19	22/09/2004	87
FU002F	*Frustulia rhombiodes* var. *viridula*	7.8	0.72	1.11	23/08/2005	87
NA003B	*Navicula shassmanii*	0.9	0.02	0.13	05/05/2004	20
NA006A	*Navicula mediocris*	0.9	0.12	0.22	22/09/2004	60
NA016A	*Navicula indifferens*	1.3	0.07	0.23	15/06/2004	40
NA033A	*Navicula subtilissima*	0.9	0.01	0.10	22/09/2004	7
NA044A	*Navicula krasskei*	1.6	0.14	0.33	22/05/2005	53
NA090A	*Navicula rotunda*	1.5	0.05	0.20	28/07/2004	27
NA160A	*Navicula submolesta*	1.0	0.04	0.15	13/07/2005	27
NA289A	*Navicula* aff. *complanata*	0.9	0.01	0.10	05/05/2004	7
NA997A	*Navicula* sp.	0.9	0.02	0.15	05/05/2004	13
NA998A	*Navicula* aff. *submolesta*	1.0	0.01	0.11	23/08/2005	7
NE003A	*Neidium affine*	0.9	0.01	0.10	22/05/2005	7
NE003B	*Neidium affine* var. *longiceps*	1.4	0.03	0.18	23/08/2005	20
NE004A	*Neidium bisulcatum*	1.0	0.09	0.21	15/06/2005	40
NI009A	*Nitzschia palea*	1.9	0.03	0.22	13/07/2005	7
PE002A	*Peronia fibula*	8.3	1.42	1.77	23/08/2005	100
PI007A	*Pinnularia viridis*	0.9	0.04	0.15	13/07/2005	27
PI015A	*Pinnularia aboujensis* var. *lacustris*	1.3	0.03	0.16	22/05/2005	20
PI015C	*Pinnularia aboujensis* var. *linearis*	1.4	0.04	0.20	15/06/2005	20
PI016A	*Pinnularia divergentissima*	0.9	0.02	0.13	22/09/2004	7
PI018D	*Pinnularia biceps* var. *pusilla*	2.4	0.21	0.41	07/09/2005	47
PI022A	*Pinnularia subcapitata*	0.9	0.08	0.19	30/06/2004	47
PI164A	*Pinnularia* aff. *terminata*	0.8	0.01	0.10	20/04/2005	7
PI995	*Pinnularia* aff. *viridis*	2.0	0.08	0.35	20/10/2004	7
PI996	*Pinnularia* unid. sp.	2.3	0.10	0.35	15/06/2005	33
SA001A	*Stauroneis anceps*	2.9	0.08	0.37	20/10/2004	40
SP005A	*Stenopterobia delicatissima*	2.2	0.07	0.12	20/10/2004	40
SP006A	*Stenopterobia curvula*	0.9	0.07	0.22	22/05/2005	47
SS002A	*Staurosirella pinnata*	12.9	1.08	2.51	22/05/2005	73
SU001A	*Suriella angustata*	0.8	0.03	0.13	07/09/2005	27
SU005Ab	*Suriella linearis* (big)	1.9	0.25	0.41	13/07/2005	67
SU005As	*Suriella linearis* (small)	11.5	0.51	1.40	20/10/2004	73
SU030A	*Suriella constricta*	1.1	0.03	0.17	13/07/2005	7
SU999A	*Suriella* sp. (v.coarse)	0.9	0.01	0.11	05/05/2004	7
TA001Z	*Tabellaria flocculosa*	92.9	24.60	21.57	25/08/2004	100
TA003A	*Tabellaria binalis*	2.9	0.10	0.41	23/08/2005	33
TA004A	*Tabellaria quadriseptata*	3.0	0.15	0.46	07/09/2005	33

Table 6.2: All diatom taxa with maximum relative abundance > 0.5% in new growth for all sites sampled. Max % = maximum % abundance of a particular taxon within a sample; avg % = mean % abundance of that taxon; sd = standard deviation; date of max % = date of maximum occurrence of the particular taxon; frequency of occurrence = percentage of sampling dates where a particular taxon was recorded.

Code	Taxon	max %	avg %	sd	date of max %	frequency of occurence (%)
AC046A	*Achnanthes altaica*	1.82	0.06	0.25	13/07/2005	38
AC046B	*Achnanthes altaica* var. *minor*	9.32	0.75	1.58	07/09/2005	77
AC134A	*Achnanthes helvetica*	20.00	3.90	4.59	15/06/2005	92
AC134C	*Achnanthes helvetica* var. *minor*	7.41	2.03	1.33	22/05/2005	85
AC134B	*Achnanthes helvetica* var.*alpina*	6.45	0.86	2.07	23/08/2005	85
AC022A	*Achnanthes marginulata*	26.07	10.99	6.92	22/09/2004	100
AC022C	*Achnanthes marginulata* var. *major*	20.00	3.09	4.72	23/08/2005	77
AC013A	*Achnanthes minutissima*	6.25	0.20	0.90	28/07/2004	62
AC143A	*Achnanthes oblongella*	4.00	0.20	0.63	13/07/2005	54
AC048A	*Achnanthes scotica*	0.62	0.04	0.13	07/09/2005	15
AU005A	*Aulacosiera distans*	1.40	0.02	0.17	13/07/2005	8
AU005E	*Aulacosiera distans* var. *nivalis*	85.71	15.47	14.85	13/07/2005	100
AU005B	*Aulacosiera distans* var. *nivaloides*	8.77	0.77	1.76	15/06/2005	77
AU9972	*Aulacosiera distans* var. *seppentrionalis*	8.96	0.81	1.40	13/07/2005	92
AU032A	*Aulacosiera lacustris*	25.53	1.25	3.42	15/06/2005	92
AU004A	*Aulacosiera lirata*	0.91	0.03	0.15	22/05/2005	15
AU010B	*Aulacosiera perglabra* var. *florinae*	3.51	0.05	0.43	15/06/2005	8
AU028A	*Aulacosiera tenella*	5.41	0.40	1.10	13/07/2005	62
BR006A	*Brachysira brebessonii*	6.25	1.16	1.58	28/07/2004	92
BR001A	*Brachysira vitrea*	3.85	0.20	0.61	25/08/2004	62
DT021A	*Diatoma mesodon*	2.22	0.15	0.54	28/07/2004	54
CM046A	*Encyonema borealis*	2.70	0.22	0.37	13/07/2005	85
EY017A	*Encyonema gracile*	0.91	0.02	0.49	13/07/2005	15
EY003A	*Encyonema hebredica*	0.93	0.06	0.12	22/09/2004	38
EY010A	*Encyonema mesiana*	1.33	0.02	0.18	13/07/2005	8
EY014A	*Encyonema perpusilla*	1.36	0.11	0.16	22/05/2005	54
EY999A	*Encyonema schubartoides*	0.92	0.03	0.32	23/03/2005	23
EY016A	*Encyonema silesiaca*	2.70	0.13	0.14	13/07/2005	23
ENC01A	*Encyonopsis* aff. *microcephala*	3.85	0.10	0.44	25/08/2004	23
EU049B	*Eunotia curvata* var. *subarcuata*	8.11	0.50	1.30	13/07/2005	62
EU015A	*Eunotia denticulata*	23.08	1.94	3.84	25/08/2004	92
EU016A	*Eunotia diodon*	0.50	0.01	0.06	07/09/2005	8
EU009A	*Eunotia exigua*	4.50	0.24	0.66	07/09/2005	62
EU047A	*Eunotia incisa*	33.33	6.08	5.54	07/09/2005	92
EU108A	*Eunotia intermedia*	2.48	0.04	0.30	15/06/2005	8
EU035A	*Eunotia major*	1.33	0.03	0.20	13/07/2005	8
EU045A	*Eunotia nymannia*	0.83	0.02	0.12	20/04/2005	8
EU040A	*Eunotia paludosa*	2.23	0.07	0.31	13/07/2005	31
EU002A	*Eunotia pectinalis*	6.45	0.16	0.82	23/08/2005	46
EU002D	*Eunotia pectinalis* var. *undulata*	2.67	0.08	0.37	13/07/2005	23

EU060Ab	*Eunotia pirla*	1.24	0.02	0.15	07/09/2005	8
EU011A	*Eunotia rhomboidea*	3.23	0.11	0.50	23/08/2005	31
EU105A	*Eunotia subarcuatoides*	19.23	3.43	3.71	25/08/2004	100
FR009A	*Fragilaria capucina*	12.82	0.28	1.60	07/09/2005	31
FR002B	*Fragilaria construens* var. *binodis*	1.49	0.02	0.18	13/07/2005	8
FR064A	*Fragilaria exigua agg*	1.56	0.04	0.22	22/09/2004	23
FR005A	*Fragilaria virescens*	14.89	1.44	2.89	15/06/2005	69
FR007A	*Fragilaria voucheriae*	4.09	0.08	0.51	20/04/2005	15
FU002B	*Frustulia rhombiodes* var. *saxonica*	2.22	0.48	0.61	28/07/2004	85
FU002F	*Frustulia rhombiodes* var. *viridula*	10.26	0.78	1.57	07/09/2005	85
GO006A	*Gomphonema accuminatum*	0.83	0.06	0.18	20/04/2005	46
NA037A	*Navicula angusta*	1.19	0.03	0.16	23/08/2005	23
NA045A	*Navicula bryophila*	0.93	0.06	0.17	22/05/2005	38
NA751A	*Navicula cryptotenella*	0.94	0.02	0.13	20/10/2004	8
NA016A	*Navicula indifferens*	16.67	0.29	2.05	07/09/2005	46
NA044A	*Navicula krasskei*	0.50	0.05	0.14	07/09/2005	31
NA006A	*Navicula mediocris*	1.93	0.07	0.27	20/10/2004	38
NA003A	*Navicula radiosa*	6.25	0.12	0.79	28/07/2004	15
NA090A	*Navicula rotunda*	0.82	0.03	0.13	23/03/2005	23
NE036A	*Neidium ampliatum*	1.42	0.07	0.25	20/10/2004	23
NE004A	*Neidium bisulcatum*	0.91	0.04	0.17	22/05/2005	15
NI009A	*Nitzschia palea*	0.93	0.01	0.12	13/07/2005	8
PE002A	*Peronia fibula*	5.50	0.87	1.36	07/09/2005	85
PI015E	*Pinnularia aboujensis* var. *lacustris*	0.92	0.03	0.14	23/03/2005	23
PI015C	*Pinnularia aboujensis* var. *linearis*	1.49	0.07	0.26	13/07/2005	31
PI164A	*Pinnularia* aff. *terminata*	0.91	0.01	0.11	22/05/2005	8
PI018D	*Pinnularia biceps* var. *pusilla*	5.00	0.27	0.79	23/08/2005	46
PI022A	*Pinnularia subcapitata*	1.20	0.05	0.19	15/06/2004	38
PI007A	*Pinnularia viridis*	0.84	0.03	0.13	30/06/2004	23
SR001A	*Staurosira construens*	1.98	0.03	0.24	15/06/2005	8
SS002A	*Staurosirella pinnata*	14.09	1.53	3.38	13/07/2005	62
SP006A	*Stenopterobia curvula*	0.96	0.03	0.14	20/10/2004	23
SP005A	*Stenopterobia delicatissima*	0.91	0.07	0.22	22/05/2005	38
SU001A	*Suriella angustata*	0.51	0.01	0.08	20/10/2004	15
SU030A	*Suriella constricta*	1.49	0.05	0.24	13/07/2005	15
SU005Ab	*Suriella linearis* (big)	5.00	0.18	0.67	23/08/2005	69
SU005As	*Suriella linearis* (small)	13.33	0.81	2.17	07/09/2005	85
TA003A	*Tabellaria binalis*	3.11	0.16	0.52	07/09/2005	31
TA001Z	*Tabellaria flocculosa*	91.35	27.59	25.42	22/09/2004	92
TA004A	*Tabellaria quadriseptata*	10.00	0.25	1.25	07/09/2005	38

The variance between site-averaged samples appears markedly less than that between the total group of samples (Figures 6.17b and 6.18b). In addition, the variance between sites is less than the total variance within the whole dataset. For both new and old growth, there is a notable distinction between samples taken on particular dates, and clear temporal associations between groups. Therefore, the major source of variance for a particular sampling date lies in the within-site distribution, i.e. between samples taken from an individual boulder (Figures 6.17a and 6.18a). The between site variance, i.e. between boulders, is comparatively small (Figures 6.17b and 6.18b), suggesting that an amalgamation of samples from around the lake littoral does provide a realistic signal of whole-lake changes, within the specific littoral epilithon habitat.

6.3.6.3 Temporal patterns in community assemblage

Monthly changes in lake-average diatom assemblage are generally associated with changes in relative abundance of a limited group of dominant taxa. The patterns are roughly similar between new and old growth, however changes are more evident in new growth assemblage. In neither old or new growth are there marked examples of species turnover within the seasonal cycle (Figures 6.19 and 6.20).

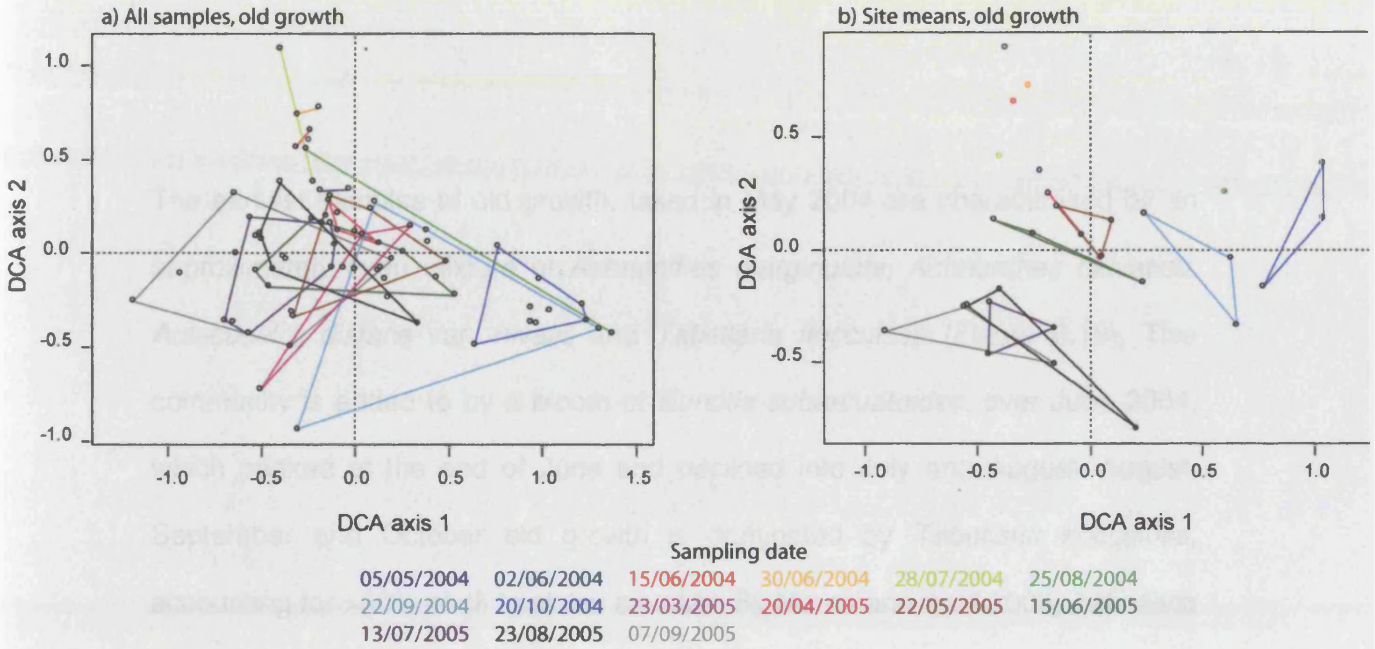

Figure 6.17: Detrended correspondence analysis of 'old growth' diatom species data (% relative abundance) for (a) all individual samples and (b) mean relative abundance for each sampling site within the lake. Coloured polygons represent the maximum range of samples taken on particular dates. Coloured points represent where only one site was sampled. In (a) variance explained by axis 1 = 0.29 and axis 2 = 0.15; in (b) variance explained by axis 1 = 0.23 and axis 2 = 0.13.

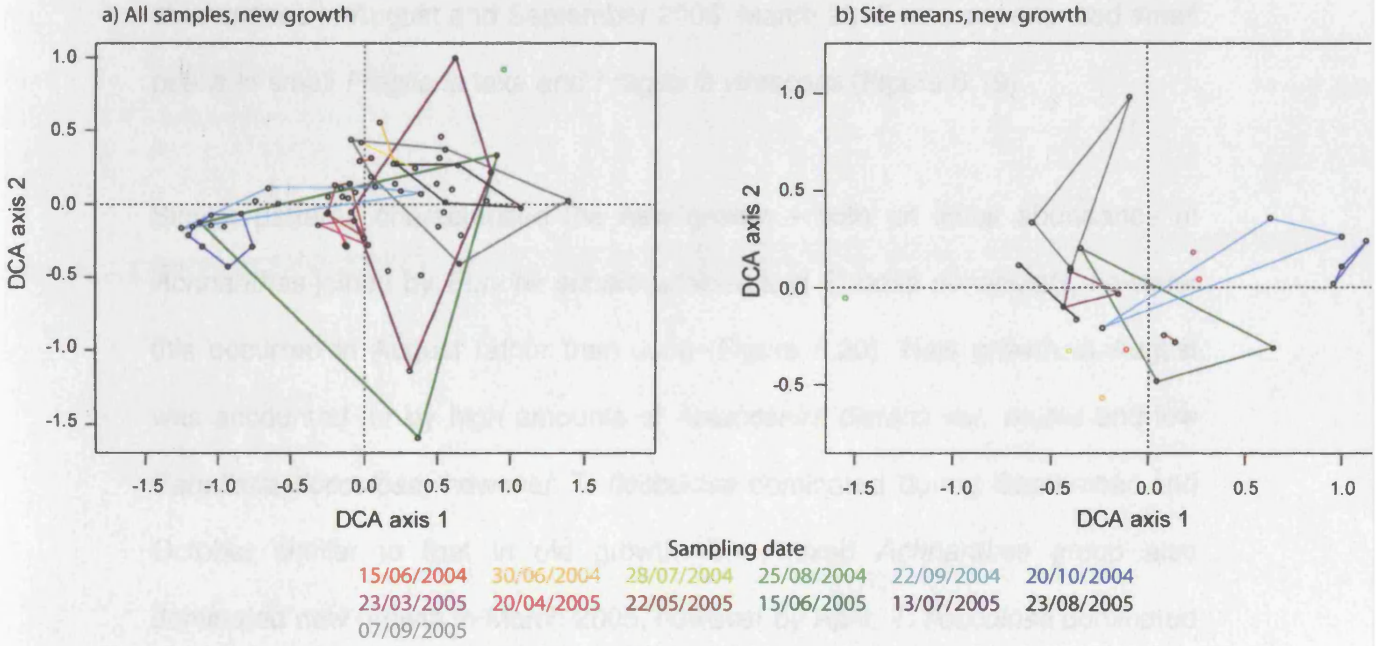

Figure 6.18: Detrended correspondence analysis of 'new growth' diatom species data (% relative abundance) for (a) all individual samples and (b) mean relative abundance for each sampling site within the lake. Coloured polygons represent the maximum range of samples taken on particular dates. Coloured points represent where only one site was sampled. In (a) variance explained by axis 1 = 0.35 and axis 2 = 0.20; in (b) variance explained by axis 1 = 0.33 and axis 2 = 0.12.

The earliest samples of old growth, taken in May 2004 are characterised by an approximately even mixture of *Achnanthes marginulata*, *Achnanthes helvetica*, *Aulacoseira distans* var. *nivalis* and *Tabellaria flocculosa* (Figure 6.19). This community is added to by a bloom of *Eunotia subarcuatoides*, over June 2004, which peaked at the end of June and declined into July and August. August, September and October old growth is dominated by *Tabellaria flocculosa*, accounting for >50% of all frustules counted. By March and April 2005, *Tabellaria* relative abundance had declined again, re-establishing the mixed community of *A. marginulata*, *T. flocculosa* and *A. distans* var. *nivalis*, with further decreases in *T. flocculosa* towards July and *A. marginulata* gradually increasing towards peak abundances in August and September 2005. March 2005 also experienced small peaks in small *Fragilaria* taxa and *Fragilaria virescens* (Figure 6.19).

Similar patterns characterised the new growth – with an initial abundance of *Achnanthes* joined by *Eunotia subarcuatoides* and *Eunotia denticulata*, however this occurred in August rather than June (Figure 6.20). New growth in August was accounted for by high amounts of *Aulacoseira distans* var. *nivalis* and low *Tabellaria flocculosa*, however *T. flocculosa* dominated during September and October similar to that in old growth. The mixed *Achnanthes* group also dominated new growth in March 2005, however by April, *T. flocculosa* dominated (>70%). This dominance fell away towards September, to be replaced again by a mixed *Achnanthes* and *A. distans* var. *nivalis* assemblage (Figure 6.20).

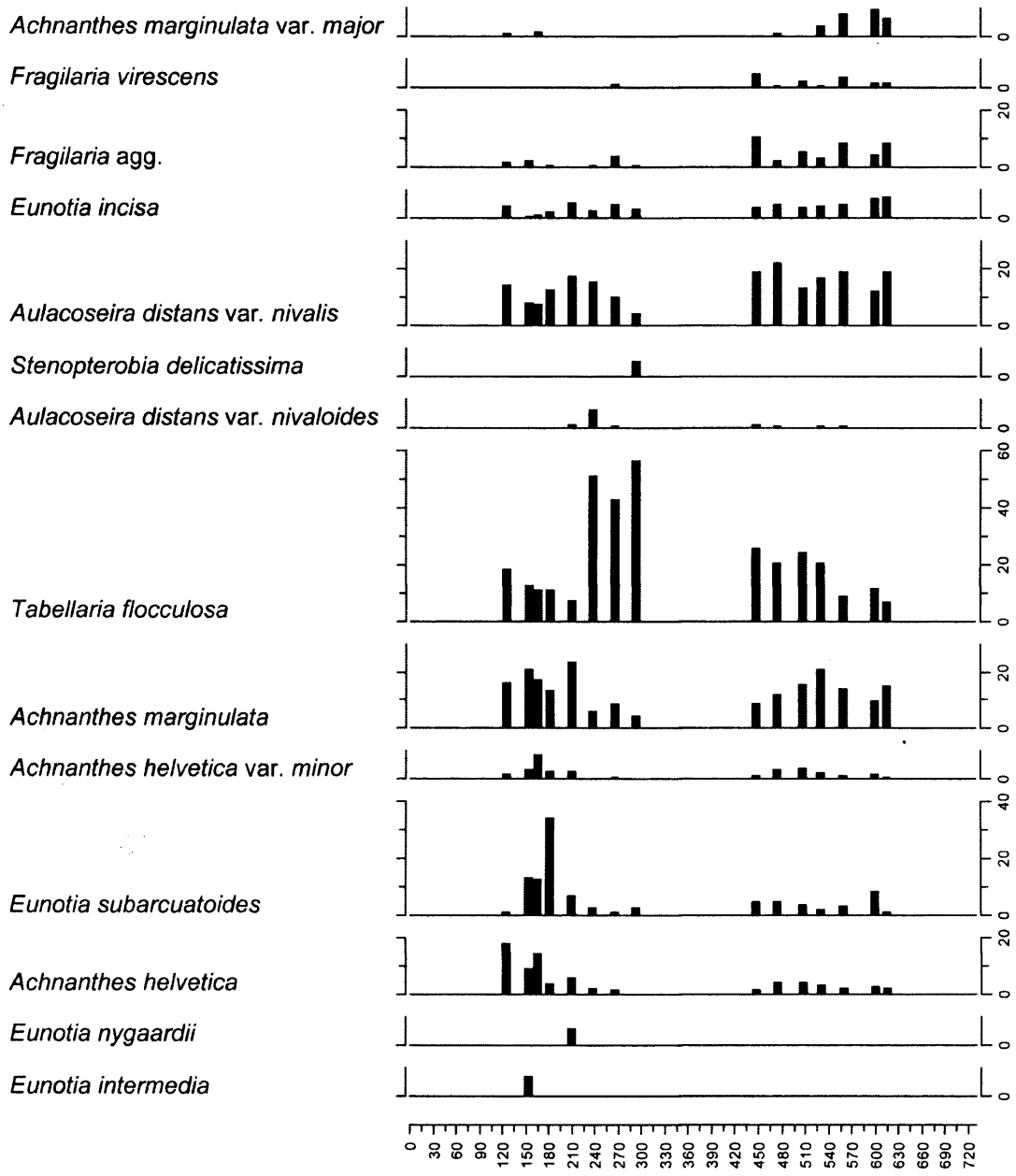

Figure 6.19: Diatom species relative abundance (%) for 'old growth' against days after 01/01/2004.

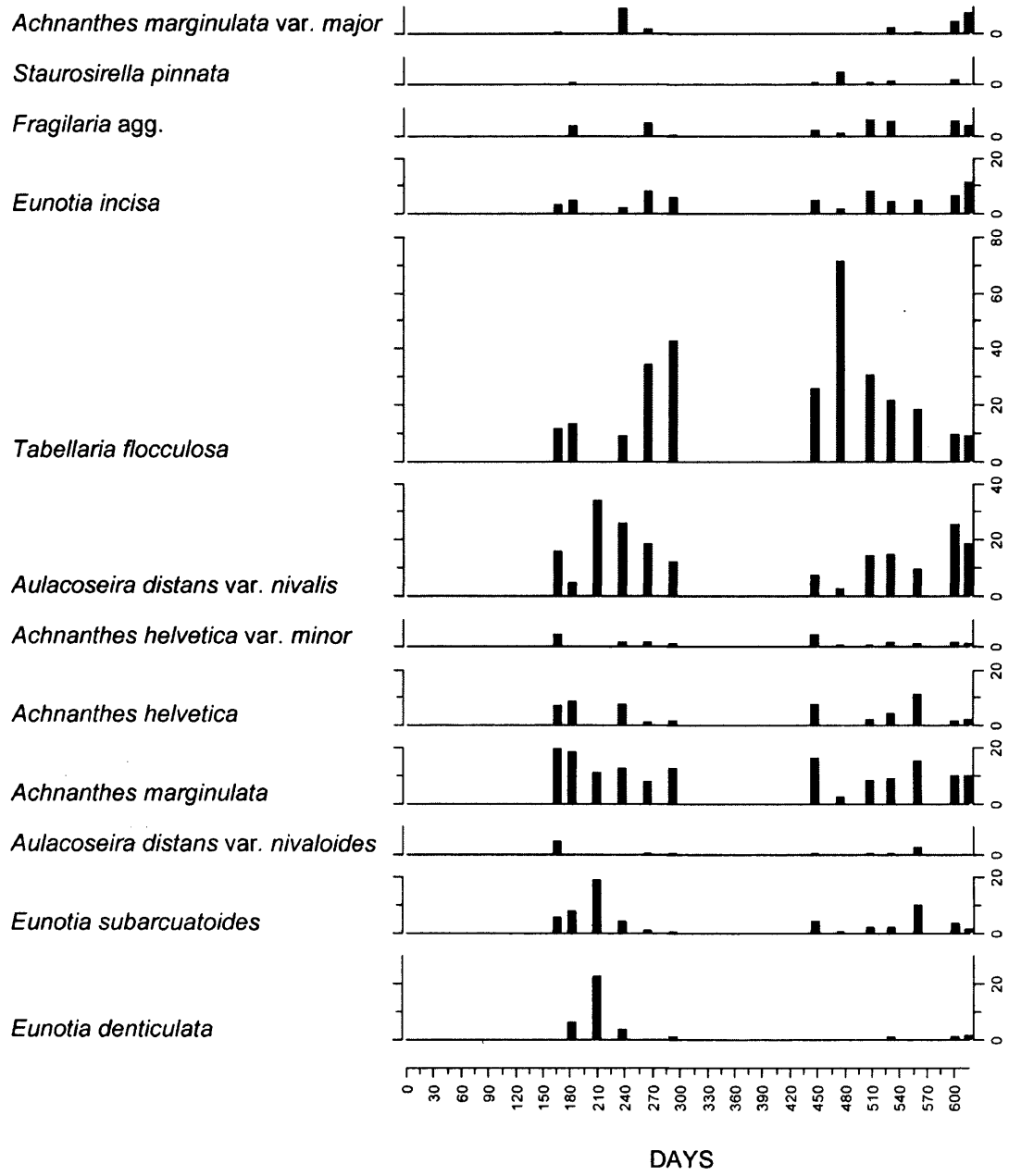

Figure 6.20: Diatom species relative abundance (%) for 'new growth' against days after 01/01/2004.

6.4 Discussion

6.4.1 Seasonal trends in diatom standing crop

Despite the apparent static nature of epilithic biofilms compared with pelagic communities, the seasonal patterns observed in diatom standing crop at Lochnagar indicates a marked dynamism in the community. Although spatial heterogeneity in epilithic diatom abundance is great, there is a clear temporal trend in lake-averaged values, whereby diatom cell densities were at a maximum during early spring (March) 2005 and minimum during the late summers (August – September) of 2004 and 2005 (Figure 6.14). Diatom cell density followed a roughly similar pattern to chlorophyll-a concentration, an indicator of total algal living biomass, suggesting that diatom standing crop size was closely associated with the overall production of the biofilm (Figure 6.14). An exception to this pattern occurred during the autumn of 2004, where high chlorophyll-a values, driven by an abundance of Chlorophyceae, coincided with overall low diatom abundance (Figure 6.14 b).

The purpose of studying the seasonal abundance of diatoms at Lochnagar was to enable an assessment of the effects of seasonal variability in diatom crop size on the transmission of climate signals through to the oxygen isotope composition of sedimentary diatom silica (Chapter 1, Section 1.5). In order to achieve this, a generalised diatom abundance curve was constructed by fitting a six-point

polynomial through the two years observations from Lochnagar (Figure 6.16). The short length of the time series collected in this study limited the development of a more sophisticated model to describe seasonal diatom production at Lochnagar, and considering the various factors which influence diatom productivity, it is extremely over-simplistic to assume such a repetitive seasonal pattern which is dependent solely on the time of year. To assume a constant seasonal pattern in diatom abundance will likely lead to considerable flaws when interpreting the sediment record. In particular the two years available data, although not exhaustive, suggest that the seasonal cycle was not identical between 2004 and 2005, both in terms of timing and extent. A more rigorous approach would be to develop mechanistic models for diatom growth in the epilithon of upland lakes such as Lochnagar, similar to those that have been derived for phytoplankton in more productive waters (e.g. Jorgensen 1995; Reynolds *et al.* 2001; Elliott *et al.* 2005). This would enable prediction of seasonal diatom biomass patterns in response to potential environmental forcing derived from independent palaeo-data or theoretical models (Elliott *et al.* 2005; Anderson *et al.* 2006). However, such models require considerable research and are currently not available for systems like Lochnagar. Therefore, in the absence of a more rigorous model, the composite curve derived from this study can still offer value as a basis for investigating the effects of seasonal diatom production on palaeolimnological records. The potential influence of different seasonal patterns in diatom standing crop on sediment $\delta^{18}O_{silica}$ records, including those observed over 2004 and 2005, are investigated further in Chapter 7.

6.4.2 Factors controlling seasonal patterns of diatom standing crop at Lochnagar

In order to appreciate the potential effects of short term intra- and inter-annual variability in diatom productivity and standing crop over lake sediment $\delta^{18}O_{silica}$ records, the factors which control diatom abundance need to be considered. In particular, changes in the physical and chemical conditions in a lake system can lead to alterations in the seasonal pattern of diatom abundance with time, thus leading to changes in the $\delta^{18}O_{silica}$ signal. The factors which control the size of diatom standing crop at any particular time can be physical (i.e. lake water temperature, solar irradiance and physical disturbance), chemical (nutrient limitation and chemical inhibition) and biological (e.g. grazing effects and competition from other algae) (Reynolds 2006). At Lochnagar, as for all aquatic systems, these three categories are intimately linked.

Water temperature and solar irradiance are important factors in regulating algal growth rate and photosynthesis, whereby warmer temperatures and increased irradiance flux usually lead to increases in growth rate and photosynthetic production, except for inhibitory effects at high levels (Round 1973; Jewson 1992; Falkowski and Raven 1997; Reynolds 2006). However, at Lochnagar, maximum diatom standing crops occur during early spring, where water temperature and light availability is low (Figure 6.15), suggesting that externally

driven temperature and light availability do not play a primary role in controlling diatom abundance. Maximum diatom standing crop occurred in March 2005, shortly after the break up of ice on the lake and the onset of lake water mixing (Figure 6.15). Ice cover and low water temperatures limit diatom growth by preventing light penetration and slowing metabolic rates, therefore the timing of ice-out can have a dominant effect on the timing of diatom productivity in arctic and alpine lakes (Lotter and Bigler 2000). In addition to the direct physical effects of ice cover, during the winter months nutrients accumulate beneath the ice. Therefore, an abundance of diatoms following the ice-out in 2005 coincided with abundance of nitrate and silica (Figure 6.15). Over the monitored period 2000 – 2005, ice out also often coincided with a pulse of phosphate to the lake waters, although this was not recorded in 2005 (Figure 6.7). It is possible that the increased availability of nutrients during this time was stimulated by the mixing of lake waters – recycling nutrients from hypolimnetic waters and surface sediments or by an increased flux of terrestrial material due to snow melt in the catchment. The latter explanation is less likely due to catchment soils usually being frozen during the early spring at Lochnagar (Jenkins *et al.* 2007). The availability, or otherwise, of phosphate (PO_4-P) fluctuates markedly throughout the record. The absence of PO_4-P spikes during the springs of 2000 and 2005 may relate to the sampling resolution (bi-weekly) being too coarse to catch the periods of detectable phosphate prior to uptake by aquatic organisms (Figure 6.7). Of particular note, however, are the phosphate peaks during the summer of 2005, which coincide with the surprising decision of the Cairngorms National Park

Authority to fertilise parts of the Lochnagar catchment (Figure 6.7). In natural circumstances therefore, physical factors appear to play an important role in driving nutrient availability within Lochnagar, and therefore can be expected to have both direct and indirect effects on diatom standing crop changes.

The removal of nitrate and silica from the water by biological uptake is evident from the progressive depletion of these resources throughout the ice-free season (Figure 6.15). SiO_2 concentrations in particular appearing closely related to the abundance of diatoms. It is possible that SiO_2 and diatom abundance may co-vary due to increased levels of diatom dissolution during periods of large diatom standing crop, however the decline in SiO_2 precedes the decline in diatom standing crop over 2005, indicating this is probably not the case. The relative importance of the major nutrients nitrate, silica and phosphate in limiting diatom productivity at Lochnagar can be investigated through analysis of their molar ratios within the lake water through time (Figure 6.8). Although SiO_2 and NO_3-N appear to decline in response to diatom uptake over the monitored period, it is unlikely that these nutrients are limiting at Lochnagar. From bioassays carried out on periphytic algae collected from a range of upland British lakes, Maberly (2002) observed P to be the most likely limiting nutrient where N:P ratios are <16, N is limiting where N:P is > 250 and co-limitation is likely (i.e. both P and N limitation) where N:P ratios fall between 16 and 250. Bioassays carried out at Lochnagar during the summer of 2005 suggest that both P and co-limitation occur within the lake periphyton (C. Curtis pers. comm. regarding S. Maberly et al. unpublished

data). Over 2000 - 2005, total and soluble N:P ratios are consistently greater than 16 and fluctuate above and below 250, suggesting that Lochnagar is generally P limited but also limited by both N and P at certain times (Figure 6.8 c). Silica is believed to be limiting to diatom growth at Si:N ratios <1 and Si:P ratios <16 (Reynolds 2006). At Lochnagar, both Si/N and Si/P ratios greatly exceed these thresholds, suggesting that silica limitation is unlikely (Figure 6.8).

Interestingly, there is no evidence for increased diatom or chlorophyll-a abundance in response to the phosphate peaks during 2005 (Figure 6.15), despite an apparent P limitation during this period (Figure 6.8). If P was limiting during this period, the increase in PO_4 should have led to an increase in periphyton chlorophyll-a (Maberly *et al.* 2002) however this did not occur. The explanation for this non-response is unclear. Measures of standing biomass (diatom cell density and chlorophyll-a) are limited in this respect, since they fail to provide information regarding the rate of algal productivity at the time of sampling. It is possible, for example, that increased productivity due to phosphate availability was offset by increased grazing of the periphyton by invertebrates. Algal growth during the summer of 2005 may have been photoinhibited by high light levels, although experiments in acid lakes in Michigan, USA revealed a positive response of algal biomass to increased irradiance (Pillsbury and Lowe 1999). Alternatively, it is possible that diatom and other algal growth at Lochnagar is limited by other micro-nutrients. For example,

Vrede and Tranvik (2006) observed Fe limitation in some alpine and boreal lakes Sweden.

6.4.3 Seasonal trends in diatom species assemblages

In order to assess potential seasonality effects on sediment records, it would be beneficial if the extent of seasonal weighting could be interpreted from the dominant diatom species found in the sediment.

Although seasonal trends in diatom cell density were marked over the two years monitoring, species assemblages display a less distinct succession – with most changes consisting of changes in relative abundance rather than species turnover patterns, which has been observed in more productive systems (King *et al.* 2002a). One explanation for the lack of marked species turnover is that the presence of stable biofilms on rock surfaces ameliorates the effects of seasonal changes in growth conditions – leading to a time-dampened community response to seasonality, as suggested by Round (1972) from studies of epipelic communities. The dynamism in terms of growth regeneration observed in this study however, suggests that this hypothesis may not be appropriate for explaining the lack of species turnover at Lochnagar. In particular, the similarity between communities colonizing recently cleaned rock substrate (new growth) and those inhabiting old growth (Figures 6.17 and 6.18) suggests that the old growth biofilms are comprised of recent growth rather than a community

developed over time. Such communities are analogous to those that develop upon sand grains (epipsammon) (Miller *et al.* 1987). Under the continual instability experienced by epipsammic communities, the accepted model of diatom colonization and succession, whereby the assemblage develops from a predominantly prostrate community towards dominance by erect and stalked forms (Hudon and Bourget 1981; Hoagland 1983; Korte and Blinn 1983) does not occur (Miller *et al.* 1987). Instead, epipsammic communities remain in a pioneer state (Miller *et al.* 1987). Of the dominant taxa in the epilithon of Lochnagar, a large proportion (*Achnanthes marginulata*, *A. helvetica*, *Eunotia incisa, E. denticulata, E. subarcuatoides*) are small, prostrate forms which attach firmly to rock surfaces. The other notable taxa, *Tabellaria flocculosa* and *Aulacoseira distans* var. *nivalis* are chain-like forms which probably do not attach to substrates but remain loosely attached by being entangled amongst other filamentous algae (Knudson 1957). Both strategies are well suited to highly disturbed conditions – either allowing flexibility and rapid re-colonisation of new surfaces, or by being firmly attached and resilient to disturbance. The epilithon habitat at Lochnagar, consisting primarily of boulders, is heavily exposed to extreme turbulence, temperature changes and ice formation. In addition, the low biomass of higher plants in the loch probably has the effect of increasing grazing pressure on the epilithic biofilm. The epilithon community in the littoral of Lochnagar reflects such perpetual instability – whereby continual re-colonisation by pioneer species characterises the temporal patterns in epilithon assemblage,

with little establishment of stable communities and therefore little species succession and turnover.

Previous studies of spatial and temporal patterns in periphytic diatom communities of oligotrophic lakes have discussed the relative importance of spatial and temporal variability in epilithon assemblage and the role of trophic state (Round 1960; Jones and Flower 1986; King et al. 2002a). Seasonal changes are clearly important in terms of diatom cell density at Lochnagar, however with respect to species assemblage, spatial heterogeneity usually accounts for as much of the variability in community composition. Such heterogeneity lends support to the perpetual instability hypothesis, since the spatial diversity reflects differing stages of community development under a wide range of localised physical and biological constraints.

6.5 Conclusion

An understanding of the extent of seasonal changes in diatom abundance is required in order to appreciate the effects of such seasonality on the oxygen isotope composition of sedimentary biogenic silica. Monitoring at Lochnagar revealed marked variability in the standing crop of diatoms upon rock surfaces, the lake's primary habitat yet a rather weak signal of seasonal species succession. Diatom standing crop was greatest in March 2005, following the break up of lake ice cover and the onset of lake water overturn. Nutrient ratios in

the lake water suggest that the lake is permanently phosphorus limited (Maberly *et al.* 2002), and it appears that mobilisation of phosphate by the initial lake overturn contributed to the peak diatom abundance in March 2005. Although no phosphate was detected in lake water during March 2005, observations made over the past five years suggest this is an important mechanism driving phosphate availability. Nitrate and silica accumulate in the Lochnagar lake water beneath winter ice cover and become progressively depleted throughout the ice-free season in tandem with a decline in diatom abundance. Diatom standing crop was low during the late summers of 2004 and 2005, with resurgent growth during the autumn of 2004. The seasonal progression of diatom standing crop is therefore a function of a combination of physical, chemical and biological factors which is likely to vary with changing external forcing, such as climate change. However, in order to assess the effect of seasonality in diatom standing crop on the $\delta^{18}O_{silica}$ signal transferred to contemporary sediments, a generalised growth curve was fitted to the two years data. Based on the observations made over 2004 – 2005, the sedimentary $\delta^{18}O_{silica}$ record at Lochnagar is heavily weighted towards early spring (March and April) lake conditions, however cooler conditions in the past may have led to a later spring diatom bloom. Further discussions with regards the effect of seasonality on the $\delta^{18}O_{silica}$ record of Lochnagar are continued in Chapter 7.

The taxonomic composition of diatom communities exhibited a weak seasonal signal, with spatial variability greater in many cases than temporal changes. It is

speculated that the unstable nature of epilithic bioflims in Lochnagar, which are subject to extreme disturbance by physical processes and invertebrate grazing, prevents development of stable communities and subsequent successional changes. Consequently, it is not possible to identify seasonally specific taxa within the sediment record at present.

In order to fully quantify the effects of short term limnological controls over diatom productivity and species composition at Lochnagar and similar sites, further research is required in the form of continued monitoring over monthly scales and at a variety of sites. Ideally, such information could be incorporated within dynamic models similar to those currently used to predict changes in phytoplankton biomass and assemblage (Elliott *et al.* 2005) which would enable past changes in the seasonal distribution of diatom contribution to lake sediments to be better evaluated.

Chapter 7:

Oxygen isotope ratios of seasonal diatom silica at Lochnagar

7.1 Rationale

Despite increasing use of oxygen isotope ratios in diatom silica, a great deal remains to be investigated concerning the fractionation of oxygen between water and diatom silica during diatom growth (Chapter 1). It is necessary to calibrate this fractionation, and specifically the temperature dependence of the fractionation factor (the temperature coefficient) if accurate palaeoclimate inferences are to be made from sediment $\delta^{18}O_{silica}$ records (Labeyrie 1974; Chapter 1). One approach for investigating the controls over $\delta^{18}O_{silica}$ is to sample living diatoms from their natural habitat, measure $\delta^{18}O_{silica}$ and compare the values with the isotope composition of ambient water (in this case lake water - $\delta^{18}O_L$) and the physical and chemical environment. The aim of this chapter is to investigate the relationship between $\delta^{18}O_{silica}$ and $\delta^{18}O_L$ through analysis of monthly diatom samples from Lochnagar. Because only a small proportion of the diatom productivity at Lochnagar occurs in the phytoplankton (Chapter 5; Flower *et al.* 2007), the sediment trap approach (e.g. Raubitschek *et al.* 1999; Moschen *et al.* 2005) is not suitable at this site. Instead, artificial substrata were used to study the isotope composition of benthic diatom silica in relation to lake water

conditions. Also, by studying the seasonal pattern of $\delta^{18}O_{silica}$, it is hoped that an improved understanding of the relationship between seasonal isotope fluctuations and the annual weighted-average flux of sedimenting diatoms can be achieved.

During sedimentation, diatom silica undergoes a maturation process, whereby in-situ condensation of hydroxyl silica (Si-OH^-) occurs to form Si-O-Si linkages (Schmidt *et al.* 2001). Opaline silica can contain ~ 30% water, which is progressively lost during this dehydroxylation (Knauth 1973). In addition, diatom silica can undergo dissolution, particularly in alkaline lakes and oceans, which is often accompanied by re-precipitation of silica within the diatom frustule (Lewin 1961). Understanding of the effects of opal maturation and dissolution on $\delta^{18}O_{silica}$ is restricted to a limited number of studies (Schmidt *et al.* 1997; Schmidt *et al.* 2001; Moschen *et al.* 2006). By comparing living phytoplankton, sedimenting diatoms and surface sediments, Schmidt *et al.* (1997) and Moschen *et al.* (2006) observed increases in $\delta^{18}O_{silica}$ of ~ 3-10‰ during sedimentation. These changes were attributed to silica maturation rather than dissolution because silica-water fractionation factors correlated with the ratio of Si-OH/Si-O-Si in the diatom silica (Schmidt *et al.* 2001). Therefore, Schmidt *et al.* (2001) concluded that $\delta^{18}O_{silica}$ values reflect the conditions at the sediment-water interface, rather than in open water. Moschen *et al.* (2006) conducted experiments on the effect of dissolution on $\delta^{18}O_{silica}$ by subjecting cultured diatoms to waters of differing pH (pH 5.6 and 9) with and without prior organic

removal treatment. For organic-free diatom silica at pH 5.6, negligible silica dissolution was measured and $\delta^{18}O_{silica}$ was not altered, regardless of the experimental duration (up to 62 days). However, at pH 9, marked dissolution occurred, resulting in a $\delta^{18}O_{silica}$ increase by ~7‰ over two days. For samples where the organic coating of the cultured diatoms was kept intact, at pH 5.6 no dissolution or $\delta^{18}O_{silica}$ changes were observed. However at pH 9, minor dissolution was accompanied by an increase in $\delta^{18}O_{silica}$ by 1.6‰. Consequently, diagenetic effects over $\delta^{18}O_{silica}$ may lead to marked alterations in the signal transmitted to the sediment. Such potential effects at Lochnagar will be addressed by comparing the $\delta^{18}O_{silica}$ of contemporary diatom silica with that of recent lake sediments, reported by Morley *et al.* (2004).

7.2 Methods

7.2.1 Sampling and preparation

Sampling and analytical methods are described in Chapter 3. To summarise, monthly diatom samples were collected from Lochnagar using large surface area polypropylene artificial substrata suspended in the loch (Figure 3.4; Chapter 3). The substrata were deployed for periods of 28 days, except between November 2004 and March 2005 where they were left to over-winter beneath the ice. Following the 28 day deployment, the substrata were replaced and transported to

the laboratory in opaque polyethylene bags where they were frozen (within two days of sampling), freeze dried and diatom matter removed using a new toothbrush and deionised water. The diatom slurry was then concentrated and freeze dried again prior to preparation for isotope analysis (Chapter 3).

Due to the low volume of biogenic silica needed for fluorination isotope analysis and the low sample volumes collected during certain months it was necessary to 'spike' some samples with a known volume of a quartz standard (NBS28), which has a known $\delta^{18}O_{silica}$. Spiking thus enabled samples to be analysed, and is a valid approach so long as the $\delta^{18}O_{silica}$ value of the 'spike' and the amount of the relative proportions of the quartz and diatom silica are accurately known. A more detailed discussion of the spiking procedure and potential errors is presented in Chapter 3, Section 3.3.2.

7.2.2 Data analysis

The major trends in the taxonomic composition of artificial substrata biogenic silica samples (including the abundance of chrysophyte cysts and *Tabellaria* girdle bands) were identified by Detrended Correspondence Analysis (DCA) (Hill and Gauch 1980; Oksanen and Minchin 1997) using the VEGAN package in R (Oksanen *et al.* 2006). The significance of the DCA axes was tested against a null-model broken stick distribution (Jolliffe 1986). For comparison with $\delta^{18}O_{silica}$

data, the mean physical and chemical variables (water temperature, $\delta^{18}O_L$, pH, conductivity) were calculated for each period of artificial substrata deployment.

The fractionation factor between diatom silica and water (α) was calculated as:

$$\alpha = (1000 + \delta^{18}O_{silica}) / (1000 + \delta^{18}O_L) \quad (1)$$

Where $\delta^{18}O_{silica}$ and $\delta^{18}O_L$ are on the V-SMOW scale (Chapter 1, Section 1.2). Following standard practice, α is presented as 10^3 ln α. This is because 10^3 ln α is roughly equal to the difference between $\delta^{18}O_{silica}$ and $\delta^{18}O_L$, thereby enabling simple calculation of the fractionation factor (Hoefs 2004).

The weighted mean $\delta^{18}O_{silica}$ for the two year monitoring period (2004-2005) was calculated using observed and predicted diatom flux and $\delta^{18}O_{silica}$ data (Table 7.1).

Based on contemporary observations (Chapter 6) diatom flux was modelled as a 6-point polynomial response to month of year:

$$D = (0.2401*m^6) - (7.8191*m^5) + (71.657*m^4) + (101.16*m^3) - (4439.7*m^2) + (18482*m) - 14368 \quad (2)$$

where D = monthly diatom flux (cells/mm^2) and m = month of year (i.e. January = 1, June = 6 and December = 12).

In addition to observed $\delta^{18}O_{silica}$ values, predictions were made from measured oxygen isotope composition of lake water ($\delta^{18}O_L$) and water temperature (T_w), using a range of potential fractionation temperature coefficients (λ) derived from the literature (Chapter 1, Figure 1.2) (where $\lambda = 0$, $\lambda = -0.2$, $\lambda = -0.35$ and $\lambda = -0.5$) and intercept values (β) equivalent to those observed from measured $\delta^{18}O_{silica}$ at Lochnagar ($\beta = +40.0$, $\beta = +41.5$, $\beta = +42.5$, $\beta = +43.5$, according to λ). Given known T_w and $\delta^{18}O_L$, and estimated λ and β, the fractionation factor (α) and $\delta^{18}O_{silica}$ of monthly diatom silica are calculated as:

$$\alpha = \exp((\lambda T_w + \beta) / 1000) \quad (3)$$

$$\delta^{18}O_{silica} = \alpha(1000 + \delta^{18}O_L) - 1000 \quad (4)$$

Mean annual $\delta^{18}O_{silica}$, weighted by monthly diatom flux in order to simulate the isotope composition of the total sedimenting material was calculated as:

$$Annual\,(\delta^{18}O_{silica}) = \frac{\sum_{m=1}^{m=12} D_m \bullet \delta^{18}O_{silica,m}}{\sum_{m=1}^{m=12} D_m} \quad (5)$$

where m is the month of the year. In order to evaluate the potential effects of changing seasonal patterns of diatom production on the $\delta^{18}O_{silica}$ values of lake sediments (Chapter 6), three hypothetical seasonal diatom growth scenarios were created. In addition to the pattern observed from the contemporary system at Lochnagar, which is dominated by spring production (Chapter 6), the

scenarios represent (i) winter/early spring diatom growth, (ii) predominantly summer diatom growth, and (iii) autumn dominated diatom growth.

7.3 Results

7.3.1 Species composition of artificial substrata isotope samples

The diatoms which colonise artificial substrata often differ from those upon naturally occurring substrata in aquatic environments due to the competitive ability of certain taxa to adhere to particular surfaces (Siver 1977; Tuchman and Stevenson 1980; Stevenson and Lowe 1986; Goldsmith 1996; 2000). However, the diatom flora sampled using artificial substrata at Lochnagar was, in general, very similar to that observed upon natural substrata (Chapter 6). The flora were characterised by a predominance of *Tabellaria flocculosa* with seasonal blooms of *Aulacoseira distans* var. *nivalis* and *Achnanthes marginulata.* The taxonomic composition of the artificial substrata samples underwent moderate change over the seasonal cycle during the two monitored years (Figure 7.1). Chrysophyte cyst abundance appears to demonstrate a recurring pattern of spring peak abundance in June 2004 and May 2005. This is consistent with phytoplankton monitoring over 1997 and 1998 (Chapter 6). *Aulacoseira distans* var. *nivalis* was abundant in the late summer (July and August) 2004, however no bloom occurred in 2005. *Tabellaria flocculosa* was most abundant during the late spring and early autumn in both 2004 and 2005, a pattern which is particularly notable

in the relative abundance of *Tabellaria* girdle bands, which could contribute considerably to the overall diatom silica flux. By contrast, *Achnanthes* (predominantly *A. marginulata,* plus *A. helvetica* and *A. helvetica* var. *minor*) mostly occurred in the late autumn (October and November) and especially early spring (March and April) 2005. *Eunotia subarcuatoides* also occurred in spring and autumn – peaking in April 2005 (Figure 7.1). DCA analysis identifies two axes which together significantly explain > 40% of the variance in the artificial substrata taxonomic data (Figure 7.2). The time series of the DCA species scores therefore offers a reliable summary of the major taxonomic changes. DCA axis 1 is predominantly driven by the balance between peak *Achnanthes marginulata* values (positive values) and chrysophyte cyst abundance (negative values) and therefore demonstrates marked peaks in March and October 2005

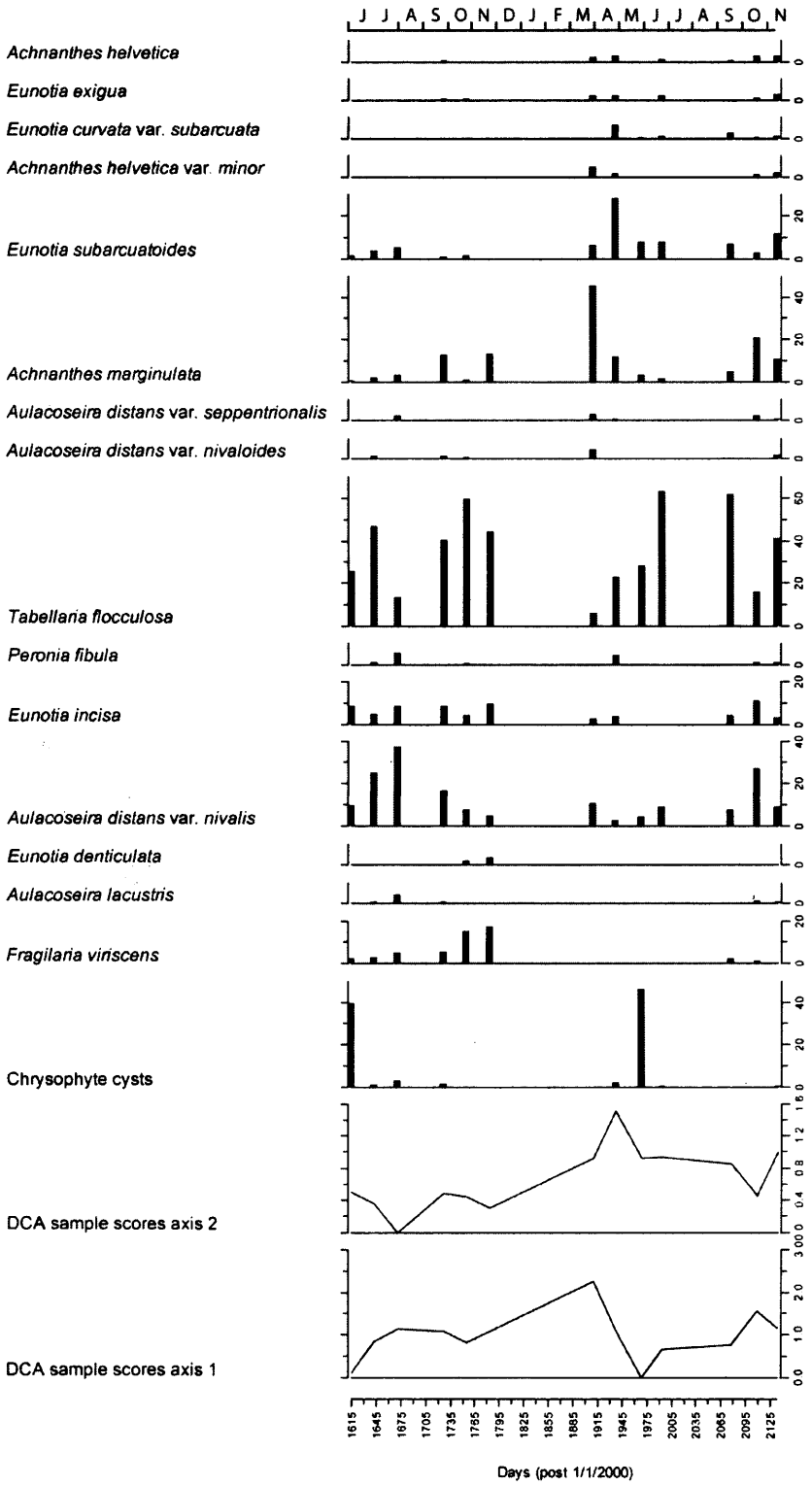

Figure 7.1: Taxonomic assemblage of artificial substrata samples deployed at Lochnagar (% relative abundance).

and troughs during June 2004 and May 2005 (Figure 7.1). DCA axis 2 responds predominantly to the relative abundance of *Aulacoseira distans* var. *nivalis* and therefore peaks in August 2004 (Figure 7.1).

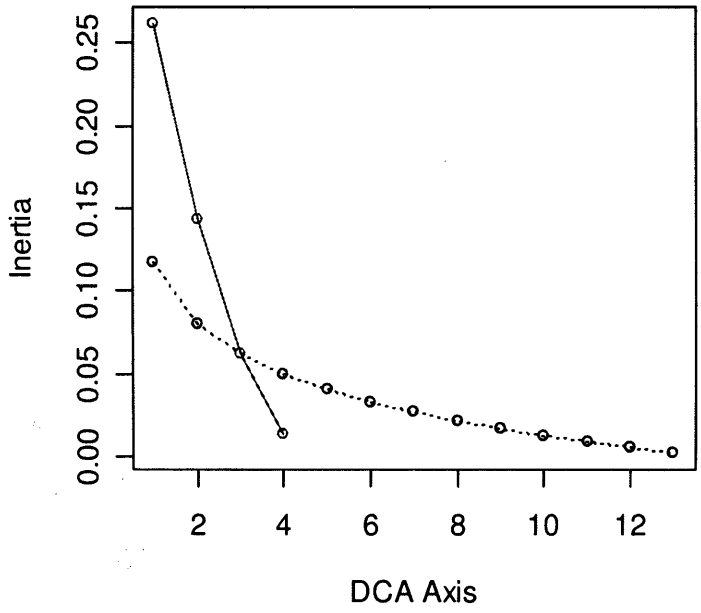

Figure 7.2: Screeplot illustrating the inertia (% of total variance) explained by cumulative detrended correspondence (DCA) axes. Solid line = inertia of Lochnagar artificial substrata taxonomic data; dashed line = random distribution of inertia, as estimated using the broken stick algorithm. Where observed inertia is greater than the broken stick, the axis explains a significant proportion of the data.

7.3.2 Oxygen isotope ratios of diatom silica: seasonal patterns

$\delta^{18}O_{silica}$ data derived from material collected monthly by artificial substrata are presented in Table 7.1 and Figure 7.3. The mass of some samples was

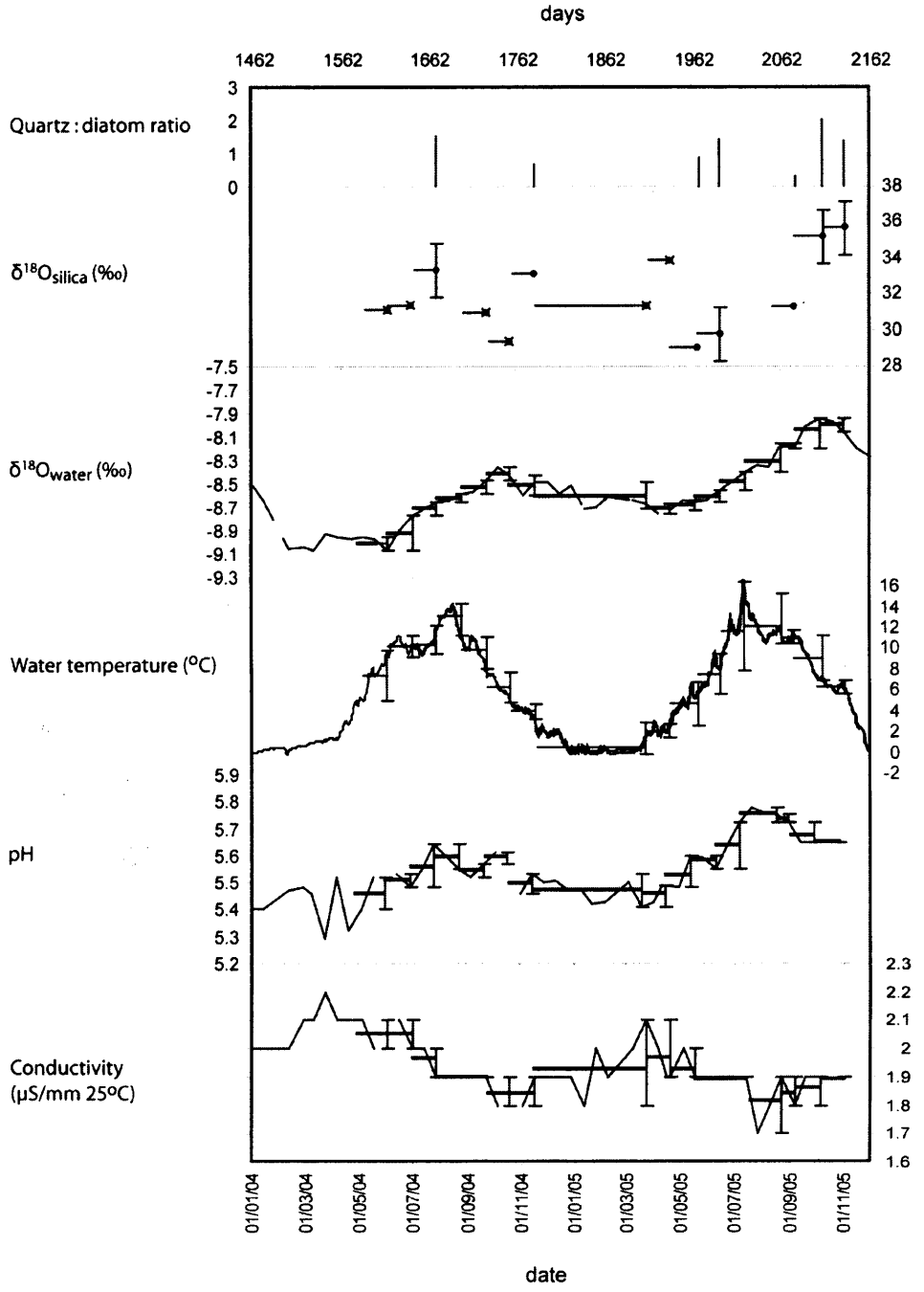

Figure 7.3: $\delta^{18}O_{silica}$ data from artificial substrate samples (crosses = samples not spiked, circles = spiked samples), compared against time with spiking amount (quartz:diatom ratio), mean $\delta^{18}O$ of lake water ($\delta^{18}O_{water}$), mean water temperature, mean pH and mean conductivity from measurements taken throughout the month preceding sampling. Horizontal bars illustrate the duration of deployment of artificial substrates and the time period for which the water chemistry and temperature data are averaged. Vertical bars for $\delta^{18}O_{silica}$ data represent an arbitrary ± 1.5‰ error range given to samples spiked with a quartz:diatom ratio <1. Vertical error bars for all other data represent the range of variation across the averaged period of time.

insufficient for standard analyses (< 5 mg) and required 'spiking' with a known amount of quartz silica to enable $\delta^{18}O_{silica}$ analysis. A preliminary experiment suggests that this approach is reasonable where the ratio of the quartz:diatom mixture is <1 (Chapter 3, Section 3.3.2). In order to highlight potential spiking errors with some samples, those samples with a quartz:diatom ratio >1 were given arbitrary ±1.5‰ error bars (Figure 7.3). Horizontal bars illustrate deployment times for artificial substrata and mean water conditions during the deployment period for all other variables. Due to exceptionally low sample volumes (total sample weight prior to silica extraction > 0.1g), no measurements were made from material sampled in August 2004, and July and August 2005. No sampling was possible during the ice-cover period between November 2004 and March 2005, therefore the sample collected in March 2005 represents accumulation over this prolonged period.

$\delta^{18}O_{silica}$ demonstrates marked variability on a monthly scale over the two monitored years, however the two years do not show similar patterns. Highest values for 2004 occurred in July and November (~ +33‰, both spiked samples), and the lowest value (+29.4‰) occurred in October (not spiked). For 2005, the highest values were observed in April (+34‰, not spiked), October 2005 and November 2005 (+35.2 and +35.7‰, both spiked). Lowest values for 2005 (+29‰) occurred in May (not spiked) (Table 7.1).

Table 7.1: Primary $\delta^{18}O_{silica}$ data collected from artificial substrata samples, measured diatom cell density data and estimated diatom abundance using Equation 2. Stars indicate spiked samples.

Sample	Sampling Date	$\delta^{18}O_{silica}$		Diatom abundance (1000 cells/mm^2)	Est. diatom abundance (% of annual total)
1	02/06/2004	31.1		1.46	8.0
2	30/06/2004	31.4		1.21	5.2
3	28/07/2004	33.3	*		3.0
4	25/08/2004			1.25	3.9
5	22/09/2004	31.0		1.52	6.1
6	20/10/2004	29.4		2.97	6.9
7	17/11/2004	33.1			4.5
8	23/03/2005	31.4		9.28	22.6
9	20/04/2005	33.9		5.77	18.0
10	22/05/2005	29.0		5.82	10.8
11	15/06/2005	29.8	*	4.84	5.2
12	13/07/2005			2.31	3.0
13	23/08/2005			1.58	3.9
14	07/09/2005	31.3		1.23	6.1
15	08/10/2005	35.2	*		6.9
16	02/11/2005	35.7	*		4.5

In theory, $\delta^{18}O_{silica}$ should reflect changes in $\delta^{18}O_L$ and water temperature. At constant temperature, an increase in $\delta^{18}O_L$ should result in a parallel increase in $\delta^{18}O_{silica}$, however with increasing temperature, the difference between $\delta^{18}O_{silica}$ and $\delta^{18}O_L$ (i.e. the fractionation factor, α) should decline. Consequently, at constant $\delta^{18}O_L$, we would expect changes in $\delta^{18}O_{silica}$ to reflect the inverse of water temperature (Clayton *et al.* 1972; Labeyrie 1974; Kawabe 1978). However, the effects of changing salinity (Taube 1954; Hoefs 2004) and pH (Mataliotaki *et al.* 2003) may introduce complications. The seasonal pattern in $\delta^{18}O_{silica}$ over the latter part of 2005 appears to reflect a magnified version of $\delta^{18}O_L$, however three winter samples (November 2004, March and April 2005) do not conform to this relationship, with high $\delta^{18}O_{silica}$ values occurring during a period of low $\delta^{18}O_L$. A relationship between $\delta^{18}O_{silica}$ and $\delta^{18}O_L$ is also not apparent for samples

collected in 2004. Water temperature, which varies annually between 0 to +14°C, appears inversely correlated with $\delta^{18}O_{silica}$ during 2005 but again this relationship is not consistent throughout. The pH of the lake water over the sampling period fluctuates between 5.3-5.8, with peaks and troughs coinciding with the seasonal temperature maxima and minima and a general increase from 2004 to 2005. Conductivity also fluctuates over the sampling period, with maxima occurring each spring, followed by a steady decline throughout the rest of the year. Conductivity values are highest in early 2004 and lowest in the summer of 2005. There is no marked similarity between $\delta^{18}O_{silica}$ and either pH or conductivity, and in particular the periods where $\delta^{18}O_{silica}$ does not correspond with changes in temperature or $\delta^{18}O_{water}$ do not relate to pH or conductivity either.

The silica-water fractionation factor (α) was calculated as a function of $\delta^{18}O_{silica}$ and $\delta^{18}O_L$ (Equation 1). Linear regression between α (presented as 1000 ln α) and mean water temperature indicates no correlation between the two (Figure 7.4). Temperature coefficients of –0.2‰/°C and –0.5‰°C - representing the range of published coefficients (summarised by Moschen *et al.* 2005) are drawn for comparison. The intercept between 1000 ln α and temperature appears to lie between +41‰ and +44‰. This is over 5‰ greater than that suggested by Moschen *et al.* (2005), whose data indicate an intercept of +37.3‰ but similar to the +41.5‰ proposed by Labeyrie's (1974) pioneering research (see Chapter 1, Figure 1.2 for a summary of previous calibration attempts). However, data from Lochnagar are scattered considerably either side of the coefficient lines. One

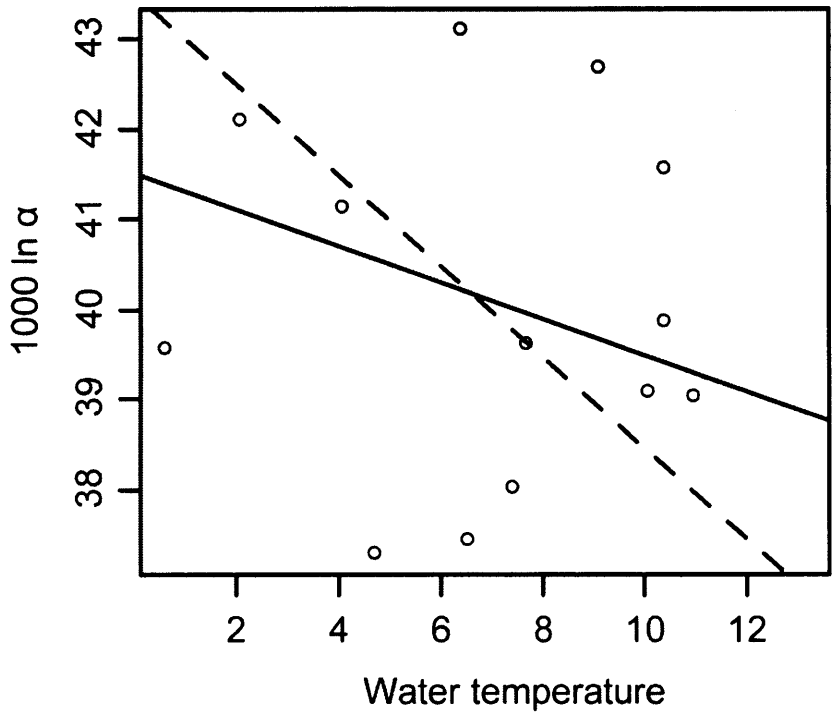

Figure 7.4: Silica-water fractionation factor (1000 ln α) between artificial substrate diatom silica and lake water against mean lake water temperature at Lochnagar. Linear regression between the two indicates no correlation. Lines illustrate potential temperature coefficients: solid line = –0.2‰/°C, dashed line = –0.5‰/°C.

potential reason for the scatter in the data is the effect of spiking only some of the samples. Three of the four samples spiked, with a quartz:diatom ratio >1, suggest fractionation factors markedly higher than the other data. By removing samples spiked with quartz:diatom ratio >1 (Figure 7.5) linear regression still indicates no correlation between 1000 ln α and temperature, however six of the nine remaining data points support a more systematic temperature coefficient. The other three points fall markedly lower, and are samples collected in October 2004, March 2005 and May 2005. In time series (Figure 7.3), these points represent notable decreases in $\delta^{18}O_{silica}$ with respect to preceding and following data points.

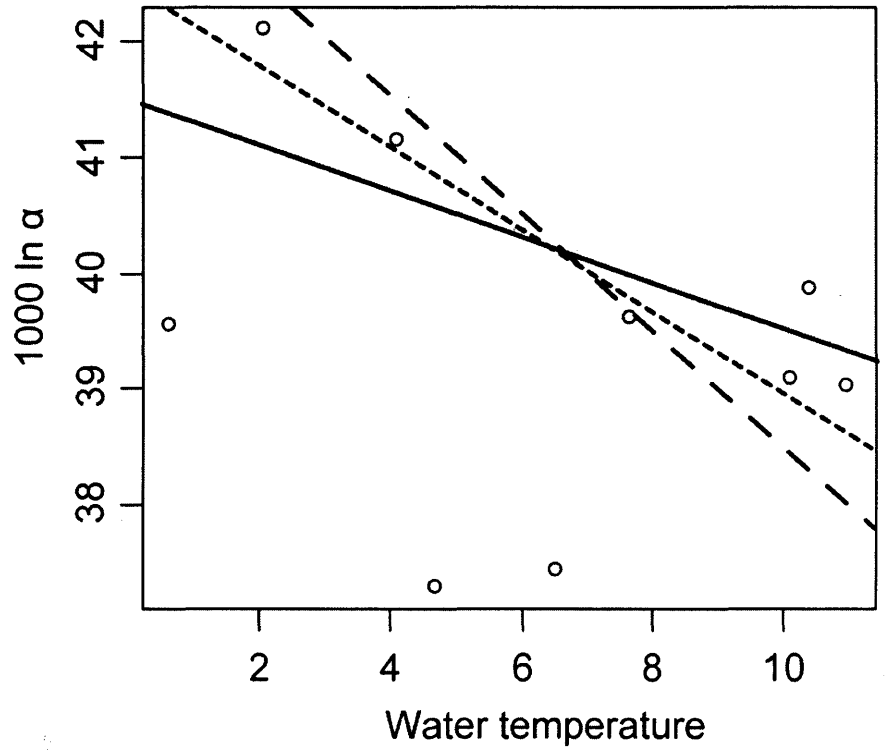

Figure 7.5: Silica-water fractionation factor (1000 ln α) between artificial substrate diatom silica and lake water against mean lake water temperature with samples spiked with quartz:diatom ratio >1 excluded. Linear regression between the two indicates no correlation. Lines illustrate potential temperature coefficients: solid line = –0.2‰/°C, dashed line = –0.5‰/°C, dotted line = –0.35‰/°C.

Interestingly, some of the marked changes in $\delta^{18}O_{silica}$ coincide with marked changes in diatom species composition (Figure 7.6). In particular, the shifts in $\delta^{18}O_{silica}$ between March and May 2005 coincides with taxonomic changes from a mixed diatom assemblage with an abundance of *Achnanthes marginulata* (March) and *Eunotia subarcuatoides* (April) to a more homogenous assemblage in May dominated by *Tabellaria flocculosa* but with a high proportion of chrysophyte cysts (Figure 7.1 and Figure 7.6). A peak in DCA axis 2 scores coincides with high $\delta^{18}O_{silica}$ values in July 2004, although this sample was spiked due to a low sample size and may be anomalous. Changes in taxonomic

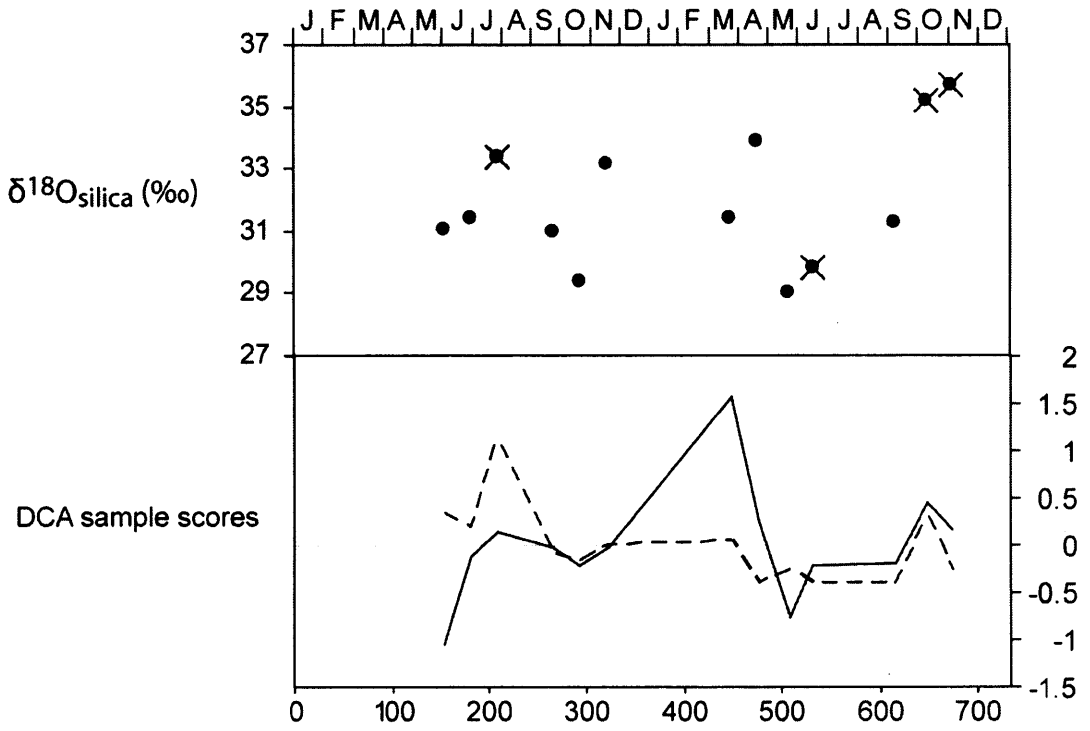

Figure 7.6: (a) Time series of $\delta^{18}O_{silica}$ from artificial substrata samples, crosses indicate spiked samples, compared with (b) taxonomic changes as illustrated by the DCA sample score axes 1 (solid line) and 2 (dotted line).

composition do not correspond with the low values indicated in Figure 7.5. A biplot of 1000 ln α against DCA axis 1 scores (Figure 7.7), excluding spiked samples, suggests a relationship between silica-oxygen fractionation and diatom taxonomic assemblage. Two samples do not conform to this relationship, however, and there is no obvious rationale for their exclusion.

7.3.3 Seasonal weighting of sediment $\delta^{18}O_{silica}$ values

Because diatom cell density was not sampled continuously, or for a full year during the two years of monitoring, estimating the weighted average $\delta^{18}O_{silica}$ of

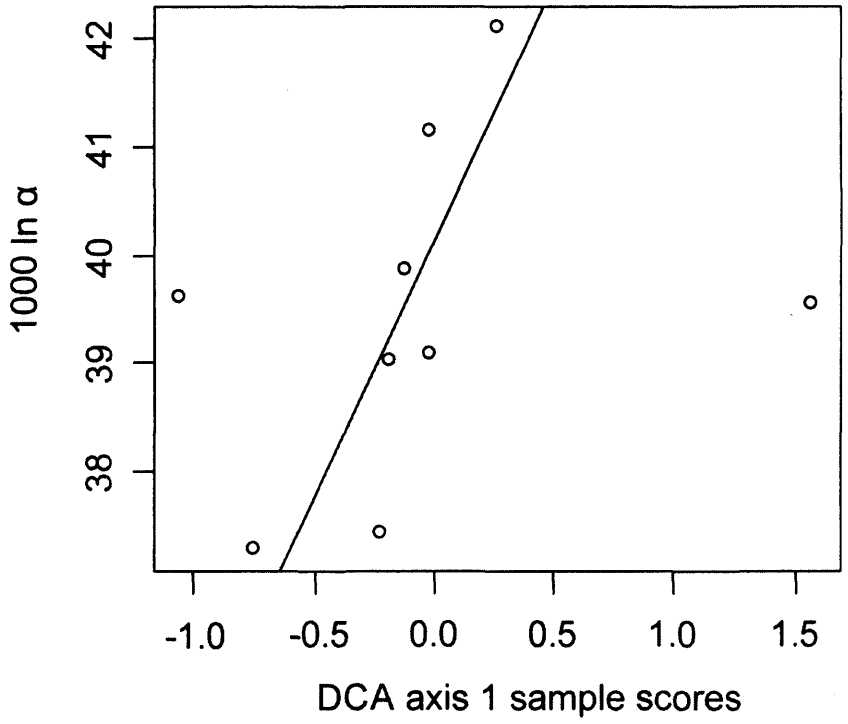

Figure 7.7: Silica-water fractionation factor (1000 ln α) against DCA axis 1 for artificial substrata samples at Lochnagar.

the diatom sedimentary flux is problematic (Chapter 6). In addition, concerns are noted (above and Chapter 3) regarding the integrity of some $\delta^{18}O_{silca}$ values measured from seasonal samples, due to spiking and other effects. In order to obtain an estimate of the weighted average $\delta^{18}O_{silica}$ of the annual diatom flux, both observed and predicted (Equation 2) diatom flux data were used. $\delta^{18}O_{silica}$ data were based on either measured values from material collected using artificial substrata at Lochnagar (Figure 7.3) or estimated $\delta^{18}O_{silica}$ values (Equations 3 and 4) according to the range of potential fractionation formulae suggested by previous research (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987; Shemesh *et al.* 1992; Brandriss *et al.* 1998; Moschen *et al.* 2005).

Estimates for annual arithmetic mean and weighted average $\delta^{18}O_{silica}$ from monthly diatom silica are presented in Table 7.2. The various input components are summarised in Figure 7.8. Estimated diatom flux (Figure 7.8 a) compares reasonably well with observed data, especially during 2005, however values for spring 2004 may be overestimated. $\delta^{18}O_{silica}$ data demonstrate marked seasonal changes, and weighted average estimates were made with and without the potentially erroneous spiked samples. Predictably, the seasonal amplitude of modelled $\delta^{18}O_{silica}$ values increases with the temperature coefficient (λ) implemented: when λ = –0.5‰/°C, $\delta^{18}O_{silica}$ values range between +29‰ and +36‰, whereas when λ is constant (0‰/°C), $\delta^{18}O_{silica}$ values vary entirely in response to $\delta^{18}O_L$ and range from +31.4‰ to +32.5‰ (Figure 7.8c).

Table 7.2: Summary of weighted mean $\delta^{18}O_{silica}$ flux for observed and modelled data for Lochnagar diatom silica, 2004 and 2005.

	$\delta^{18}O_{silica}$ data	**Diatom flux data**	**Arithmetic mean $\delta^{18}O_{silica}$**	**Weighted mean $\delta^{18}O_{silica}$**
A	*All observed data*	*Modelled*	+32.0	+31.9
B	*All observed data excluding spiked samples with quartz:diatom ratios >1*	*Observed (2004-2005)*	+31.3	+31.0
C	*All observed data excluding spiked samples with quartz:diatom ratios >1*	*Modelled*	+31.3	+31.4
D	*Model: λ = 0‰/°C, β = 40‰*	*Modelled*	+31.9	+31.8
E	*Model: λ = –0.2‰/°C, β = 41.5‰*	*Modelled*	+32.3	+32.5
F	*Model: λ = –0.35‰/°C, β = 42.5‰*	*Modelled*	+32.5	+32.9
G	*Model: λ = –0.5‰/°C, β = 43.5‰*	*Modelled*	+32.7	+33.3
	Morley et al. 2004	*Recent sediment*		+26.5
	Morley et al. 2004	*Recent sediment*		+27.3

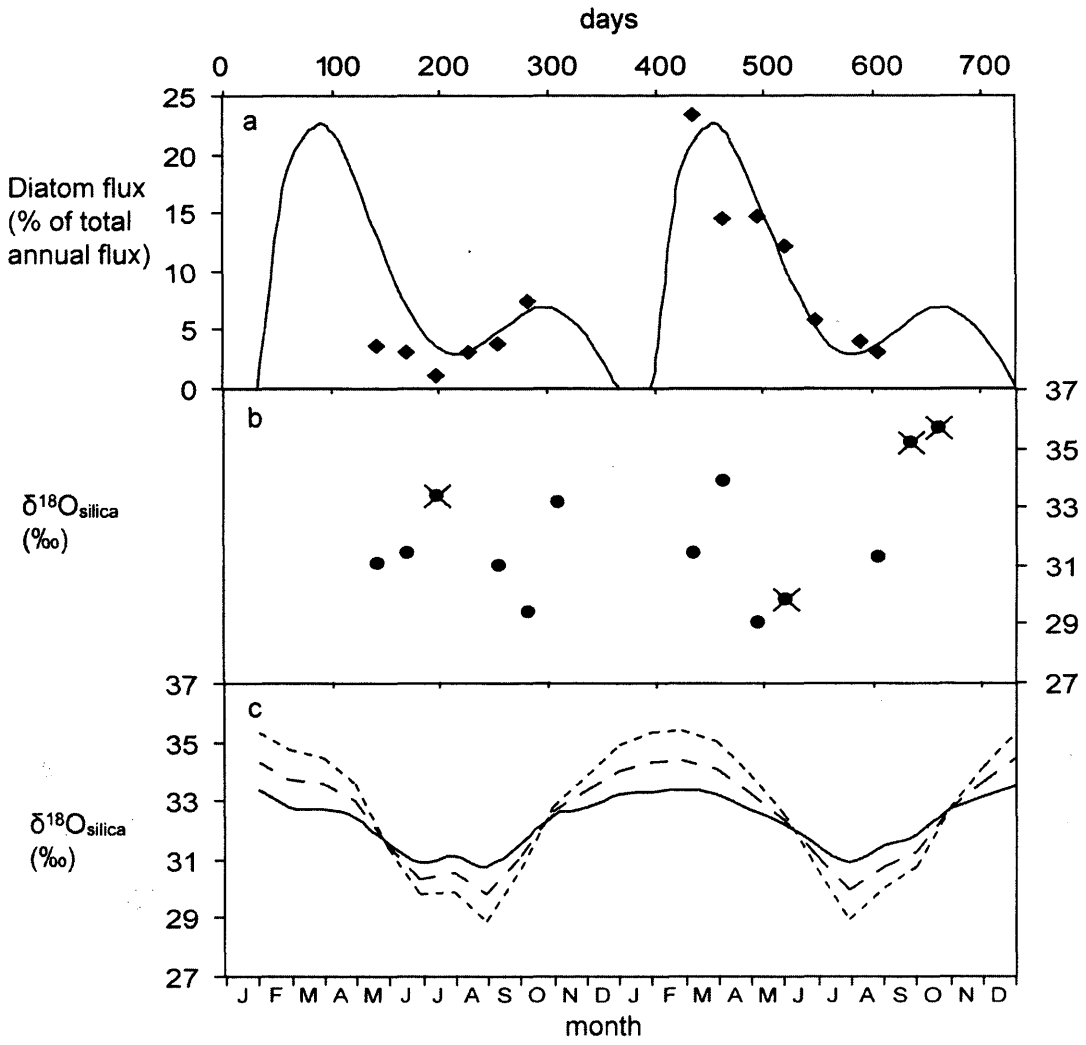

Figure 7.8: Seasonal diatom flux and $\delta^{18}O_{silica}$ for 2004-2005 at Lochnagar. (a) Modelled (solid line) and observed (filled diamonds) monthly diatom flux, both expressed as % of total annual diatom flux; (b) observed $\delta^{18}O_{silica}$ for artificial substrata diatom samples from Lochnagar – crosses indicate spiked samples with quartz:diatom ratios >1; (c) modelled estimates of monthly $\delta^{18}O_{silica}$ where (i) $\lambda = -0.2‰/°C$ and $\beta = 41.5$ (solid line), (ii) $\lambda = -0.35‰/°C$ and $\beta = 42.5$ (dashed line) and (iii) $\lambda = -0.5‰/°C$ and $\beta = 43.5$ (dotted line).

The effect of weighting $\delta^{18}O_{silica}$ by diatom flux is not marked on observed Lochnagar data (scenarios A-C, Table 7.2). Mean and weighted mean values for all data (scenario A, Table 7.2) and estimates which exclude the spiked values (scenario C, Table 7.2), where estimated diatom fluxes are used, differ by less

than 0.1‰ which is within analytical error (~0.3‰). Where observed fluxes are used – further reducing the sample size – the weighted mean is 0.3‰ less than the arithmetic mean $\delta^{18}O_{silica}$, only slightly less than the range of analytical error. Modelled $\delta^{18}O_{silica}$ values using intercepts (β) based on observed data (Figure 7.3) are higher, with arithmetic means ranging from +31.9‰ (scenario D – λ = 0‰, β = +40‰, Table 7.2) to +32.7‰ (scenario G – λ = –0.5‰, β = +43.5‰, Table 7.2). All estimates (scenarios A-G) using both observed and modelled values, predict sediment $\delta^{18}O_{silica}$ values 3.7-6.8‰ greater than the +26.5-+27.3‰ measured from recent Lochnagar sediments (Morley *et al.* 2004).

In order to explore the potential effects of changing seasonal diatom abundance patterns, three hypothetical diatom production scenarios were created for comparison with observations made at Lochnagar over 2004 and 2005 (Figure 7.9). The hypothetical patterns represent (i) an enhanced winter diatom bloom (Figure 7.9 b) – a possible occurrence during conditions of earlier ice-out (Chapter 6), (ii) a summer bloom, which might occur during a period of prolonged increased lake ice cover (Figure 7.9 c) and (iii) an enhanced autumnal bloom, which may occur during a period of enhanced autumnal lake water mixing and nutrient re-suspension (Figure 7.9 d). The hypothetical scenarios, in addition to that based on observed data (Equation 2, Figure 7.8) were used to predict surface sediment $\delta^{18}O_{silica}$ values representing the annual weighted average of monthly values (Figure 7.10). The calculations suggest that changes in the seasonal distribution of diatom production can lead to marked alterations in the

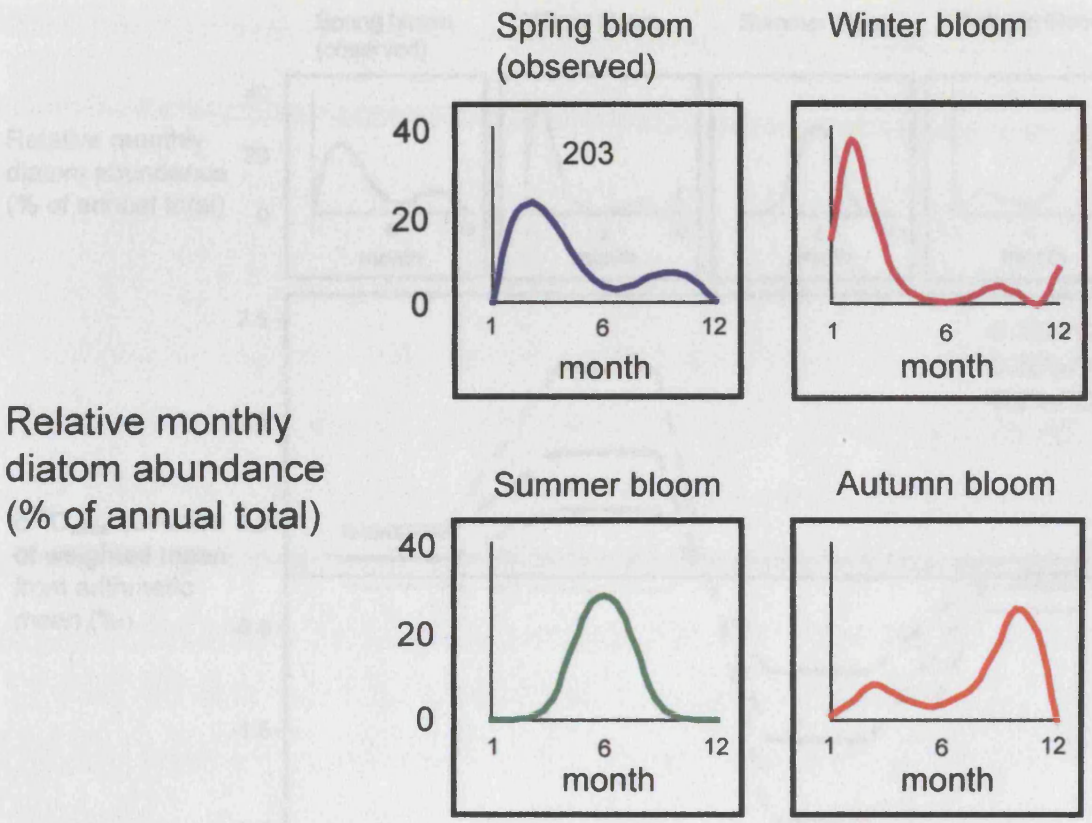

Figure 7.9: Hypothetical seasonal diatom abundance patterns used in model.

eventual $\delta^{18}O_{silica}$ values of sedimentary diatom silica (Figure 7.10). The winter bloom hypothesis causes an increase in $\delta^{18}O_{silica}$ by almost +2.5 ‰ compared to a null-model of constant diatom production throughout the year (Figure 7.10). By contrast, the summer bloom hypothesis causes a decrease in $\delta^{18}O_{silica}$ by ~ –2.5 ‰ (Figure 7.10). The spring (observed) and autumnal blooms lead to less marked alterations, which are within analytical error (±0.3 ‰) except where a temperature fractionation coefficient (λ) > 0.35 ‰/°C is used. As noted above from observed data, increasing λ leads to a marked increase in the range of predicted $\delta^{18}O_{silica}$ values and with a greater importance of seasonal effects

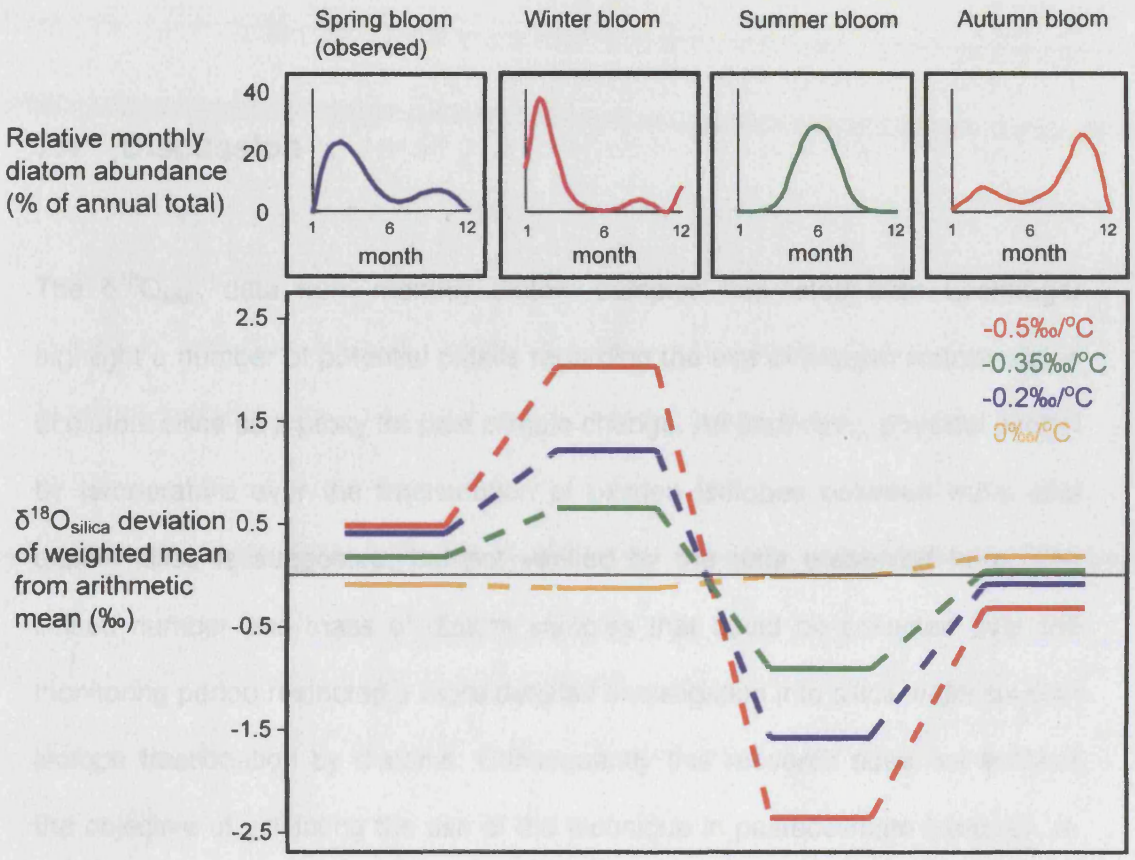

Figure 7.10: Effects of changing seasonal diatom abundance pattern on mean sediment $\delta^{18}O_{silica}$.

(Figure 7.10). Where $\lambda = 0$ is assumed, the effects of seasonality are negligible, and where $\lambda = -0.2$ ‰/°C is assumed, the summer and winter bloom hypotheses (Figure 7.10) lead to modifications in $\delta^{18}O_{silica}$ by ~ ±0.6‰, only slightly greater than analytical error.

7.4 Discussion

The $\delta^{18}O_{silica}$ data from monthly diatom samples harvested from Lochnagar highlight a number of potential pitfalls regarding the use of oxygen isotope ratios of diatom silica as a proxy for past climate change. An underlying physical control by temperature over the fractionation of oxygen isotopes between water and diatom silica is suggested, but not verified by the data presented here. The limited number and mass of diatom samples that could be collected over the monitoring period restricted a more detailed investigation into silica-water oxygen isotope fractionation by diatoms. Consequently this research does not achieve the objective of validating the use of the technique in palaeoclimate research. In hindsight, an oligotrophic system such as Lochnagar which receives a significant flux of weathered mineral silica, coupled with low diatom productivity and a diatom flora dominated by taxa with small dimensions (commonly < 20 µm) is not as ideally suited to investigating contemporary $\delta^{18}O_{silica}$ dynamics as it is to addressing issues concerning isotope hydrology and climate interactions (Chapters 4 and 5).

7.4.1 Artificial substrata taxonomic composition

The monthly-scale variability in diatom taxonomic assemblage of artificial substrata samples demonstrates a close similarity with those of natural substrata (Chapter 6). The seasonal changes on the artificial substrata are in many ways

smoother than those observed on natural substrata – probably relating to the homogeneity of the artificial substrata surface (compared to natural granite boulders) and the amalgamation of larger volumes of sample material. In particular, from the artificial substrata data, seasonal preferences are more evident for the major diatom taxa – *Tabellaria flocculosa* (late spring, early autumn); *Achnanthes marginulata* (early spring, late autumn) and *Aulacoseira distans* var. *nivalis* (late summer), as well as chrysophyte cyst production (early summer). Further monitoring over a longer timescale is required in order to fully characterise the epilithon seasonal succession. However, the data presented here support the use of artificial substrata as an adequate and replicable approach to carrying out such monitoring.

7.4.2 Natural and artificial controls over seasonal $\delta^{18}O_{silica}$ patterns

A pilot study into the applicability of spiking samples to enable analysis of small samples revealed that the approach is useful where the weight of the quartz spike is less than that of the original diatom sample (i.e. quartz:silica ratio < 1), however caution must be used (discussed in detail in Chapter 3). The amount of weighing error is directly proportional to the amount of diatom silica relative to quartz. Therefore, the accuracy of estimated $\delta^{18}O_{silica}$ values declines considerably with decreasing diatom amount (Chapter 3, Section 3.3.2).

Due to the limited number of $\delta^{18}O_{silica}$ analyses achieved through sampling in Lochnagar, a rigorous assessment of the fractionation of oxygen isotopes between diatom silica and lake water was not possible. However, when the heavily spiked samples are removed, it would appear that six of the nine remaining samples support a linear temperature coefficient of ~–0.3‰, not too dissimilar to the –0.2‰ fractionation coefficient suggested in the recent literature (Brandriss *et al.* 1998; Moschen *et al.* 2005). Potential reasons for anomalous values from these samples include contamination, species effects and the result of chemical effects such as changing lake water pH. There is no clear evidence for contamination in any of the samples analysed. However, due to the small size dimensions of the majority of diatoms within the samples and the overall low sample volumes, sieving was not carried out in the preparation procedure. As a consequence, the final samples were rich in fine grade matter. This fine matter was identified using plain and cross-polarised microscopy as broken diatom fragments, however it is possible that some minerogenic clay particles could have been missed by the screening. Elemental analysis of biogenic silica samples from Lake Baikal, deemed pure following microscopic analysis, has revealed the presence of minerogenic material agglomerated with diatom frustules, confirmed by scanning electron microscopy (M.J. Leng pers. comm.). This study highlighted the limitations of screening diatom samples using optical microscopy alone, and some minerogenic contamination can not be discounted from the samples from Lochnagar. Such contamination may have contributed to the isotope signals from some or all of the samples. Because optical microscopy

can not detect such contaminants, it is suggested that elemental analyses are conducted routinely in future for the screening of biogenic silica samples (e.g. Brewer *et al.* 2007; Lamb *et al.* 2007).

Of the other potentially confounding factors, none demonstrate a clear association with $\delta^{18}O_{silica}$ or the offsets observed (Figure 7.5). For example, pH effects the relative abundance of dissolved silica species present in water (Mataliotaki *et al.* 2003). In addition, increasing pH and conductivity would indicate an increase in the potential for diatom silica dissolution. However, neither pH or conductivity vary considerably over the monitored period, nor do they readily correlate with changes in $\delta^{18}O_{silica}$. Consequently appears that changing pH and/or dissolution effects do not explain a lack of thermal dependence in $\delta^{18}O_{silica}$.

The taxonomic composition of the biogenic silica samples did vary over the monitored period – in particular the abundance of chrysophyte cysts within June samples from each year represents a contribution by a completely different algal group which potentially could have a marked effect on isotope fractionation. In addition, Chrysophyceae (and to some extent *Aulacosiera*), grow suspended in the pelagic zone of Lochnagar (Chapter 6, Figure 6.2) and hence potentially record different $\delta^{18}O_L$ and temperature conditions. However, the effect of changing taxonomic composition does not appear to correlate with the offsets observed in Figure 7.5. There does appear to be some correlation between DCA

axis 1 scores (a summary of major taxonomic change) and oxygen isotope fractionation factor (Figure 7.7), however this correlation is not consistent for all samples and it is impossible to interpret a causative relationship due to the autocorrelation of both $\delta^{18}O_{silica}$ and DCA axis 1 with other seasonal lake changes. Overall, a taxonomic control over diatom isotope fractionation is less logical than a thermal effect. Swann et al. (2007) observe $\delta^{18}O_{silica}$ offsets between different size fractions of ~ 1.2‰ suggesting that species composition may have an effect over $\delta^{18}O_{silica}$ profiles. However, there has been no evidence to date from any previously published sedimentary $\delta^{18}O_{silica}$ profile which suggests a correlation between $\delta^{18}O_{silica}$ and the diatom taxonomic assemblage (Barker *et al.* 2001; Leng *et al.* 2001; Shemesh *et al.* 1995; Shemesh and Peteet 1998; Jones *et al.* 2004; Rosqvist *et al.* 2004; Morley *et al.* 2005).

Although the data from Lochnagar suggest some degree of similarity in the temperature dependence of silica-water fractionation with recently published coefficients (Brandriss *et al.* 1998; Moschen *et al.* 2005) (Figure 7.5), there is a marked disparity in the estimated constant fractionation factor, which for Lochnagar appears to be ~ +41‰, similar to that observed by Labeyrie (1974) (Figure 7.5). This is ~ 5‰ greater than that observed by Moschen *et al.* (2005) at Lake Holzmaar. Indeed, the range of published constant fractionation factors is large (Chapter 1, Figure 7.2) and therefore requires greater attention in the future. To some extent, the intercept between 1000 ln α and temperature is dependent on the slope of the regression – inevitably very few researchers

analyse diatom silica produced at 0°C, conditions at which diatom productivity is very low, so published intercepts are predominantly estimated by extrapolation of data collected at higher temperatures. Prior to this research, it would appear that data collected in marine environments are associated with higher constant fractionation factors (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987; Matheney and Knauth 1989; Shemesh *et al.* 1992) than those produced for freshwater taxa (Brandriss *et al.* 1998; Moschen *et al.* 2005), however data from Lochnagar compare more favourably with marine studies. Clearly, further research is required in order to identify the processes which control not only the slope of the temperature-fractionation response, but also to assess the degree of constant offset between $\delta^{18}O_{silica}$ and the isotope composition of formation water.

7.4.3 Seasonal effects on weighed average sedimentary records

Although the contemporary $\delta^{18}O_{silica}$ data from Lochnagar are far from convincing, there is some indication that a systematic, temperature dependent fractionation may take place between diatom silica and water – supporting previous research (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987; Matheney and Knauth 1989; Brandriss *et al.* 1998; Moschen *et al.* 2005). In order to assess the contribution of seasonal diatom productivity and isotope fractionation towards the formation of the sediment record, the weighed mean $\delta^{18}O_{silica}$ of the annual diatom flux was estimated. In most cases, the effect of weighting the annual average $\delta^{18}O_{silica}$ by monthly diatom productivity is not marked (Table 7.2). The

temporal coverage of observed diatom productivity is not as extensive as estimated diatom flux (using Equation 2) and consequently the predicted diatom production tends to exaggerate seasonal effects compared to observed data. Seasonality becomes a factor only when a thermal fractionation coefficient (λ) is implemented: where $\lambda = 0$ (scenario D, Table 7.2) the effect of weighting falls within the realms of analytical error. Scenario D (Table 7.2) represents the sole effects of changing $\delta^{18}O_{water}$, hence despite marked seasonal changes in $\delta^{18}O_{water}$ (Chapter 5), the effects will not be significant, beyond analytical error, to weighted-average sediment $\delta^{18}O_{silica}$ values (Scenario D, Table 7.2). However, such effects may be important in smaller lakes, or evaporative systems, where monthly changes in $\delta^{18}O_{water}$ are more marked. Increasing the thermal fractionation coefficient ($\lambda > -0.2‰/°C$) increases the importance of seasonality on the sediment record. A thermal coefficient of $\lambda = -0.5‰/°C$ would lead to a maximum offset of –0.6‰, which although not very large is equivalent to an inferred reduction of annual lake water temperature by 1°C under constant conditions.

Variability in the seasonal pattern of diatom production can have important effects on the $\delta^{18}O_{silica}$ value of sedimentary diatom silica, especially if a large thermal coefficient ($\lambda = -0.5‰/°C$) is operational (Figure 7.10). By weighting diatom production towards summer or winter conditions, the sedimentary $\delta^{18}O_{silica}$ value can vary by ± 2.5‰. Such changes can be expected to occur in response to natural environmental changes – the timing of ice break up, for

example, appears instrumental in determining the timing of maximum diatom production (Chapter 6). Within contemporary high alpine lakes in the Swiss Alps, for example, diatom production is restricted to a short period during the summer by the presence of ice cover throughout much of the year (Lotter and Bigler 2000). Due to the cyclical nature of $\delta^{18}O_L$ and water temperature changes throughout the year (Chapter 5), diatom production during the autumn or spring, such as occurs in the contemporary Lochnagar system, tends to reflect the mean annual conditions to a greater extent (Figure 7.10). The combined importance of water temperature, $\delta^{18}O_L$ and the timing of diatom production on $\delta^{18}O_{silica}$ values highlights the need for a more holistic approach to interpreting lake sediment records. This issue is discussed further in Chapter 9.

The most striking observation to be drawn from the $\delta^{18}O_{silica}$ averages (Table 7.2) is the marked difference between $\delta^{18}O_{silica}$ measured from the artificial substrata samples and recent lake sediments from Lochnagar (measurements made by Morley *et al.* 2004). The sediment $\delta^{18}O_{silica}$ values of Morley *et al.* (2004) are 3.7 to 6.8‰ lower than those analysed from living diatoms collected by artificial substrata. Assuming the maximum hypothetical fractionation coefficient ($\lambda > -0.5$‰/°C), this offset is equivalent to a decrease in water temperature by 10°C between lake sediment deposition and the onset of diatom sampling in 2004. Alternatively, the offset equates to an increase in lake water $\delta^{18}O$ by 5‰. Following the traditional approach of Dansgaard (1964) and Yurtsever (1975), supported by analysis of contemporary $\delta^{18}O_P$ data at Lochnagar (Chapter 4), a

5‰ change in $\delta^{18}O_P$ is equivalent to a increase in air temperature of 7-10°C. Yang (2000) estimates that the sediments analysed by Morley were deposited late in the 19th century (Yang 2000). However, instrumental climate data for the UK does not demonstrate such marked temperature changes (Manley 1953; 1974; Parker *et al.* 1992) and neither do reconstructed temperature values for Lochnagar, derived by extrapolation and taking into account altitudinal effects (Agusti-Panareda and Thompson 2002; Chapter 1). Although the sediment samples were carefully screened prior to analysis – as part of an investigation into cleaning methods (Morley *et al.* 2004), clay contamination is possible (discussed above). However, unlike the contemporary samples analysed in this study, the surface sediments were sieved several times at 10 μm, and are therefore less likely to contain many minerogenic matter, except for those trapped within or adhered to the surface of diatom frustules (Morley *et al.* 2004). It is therefore logical to assume that some of the observed difference between contemporary (artificial substrata) and sediment $\delta^{18}O_{silica}$ relates to an additional, diagenetic process such as dehydroxylation or dissolution.

The offset between contemporary and sediment $\delta^{18}O_{silica}$ at Lochnagar is opposite to that observed by Moschen *et al.* (2006) at Lake Holzmaar, Germany, and between contemporary diatom $\delta^{18}O_{silica}$ and marine surface sediments (Schmidt *et al.* 1997). In both these cases, sedimentation appeared to cause an increase in $\delta^{18}O_{silica}$. Post-depositional $\delta^{18}O_{silica}$ increase was correlated with internal structural and compositional changes in the diatom silica, arising from in-

situ condensation of Si-OH groups and formation of Si-O-Si linkages (Schmidt *et al.* 2001; Moschen *et al.* 2006). Dissolution can also lead to marked alterations in $\delta^{18}O_{silica}$ (Moschen *et al.* 2006), however the effects are minimal where organic matter remains largely in tact during sedimentation (as generally occurs in natural systems) and at the average pH of Lochnagar lake water (~5.6), dissolution effects are unlikely (Moschen *et al.* 2006). One potential explanation for a lowering of $\delta^{18}O_{silica}$ between contemporary and sedimentary diatom silica is the re-equilibration of diatom silica with ^{18}O depleted hypolimnetic waters (Moschen *et al.* 2006). However, Lochnagar is well mixed for most of the year and either water temperatures or $\delta^{18}O_{water}$ in the lake bottom would need to differ markedly from epilimnetic conditions in order to explain the considerable offset between contemporary and sedimentary diatom silica. Consequently, it would appear that dehydroxylation effects are more likely to explain the disparity in $\delta^{18}O_{silica}$ between contemporary and sedimentary diatoms at Lochnagar. However, the difference between the data from Lochnagar, where sediment $\delta^{18}O_{silica}$ values are lower than contemporary values and previous examples of $\delta^{18}O_{silica}$ increase during sedimentation (Schmidt *et al.* 2001; 2006; Moschen *et al.* 2006) requires consideration. Unlike the contemporary samples of (Moschen *et al.* 2005; 2006), where traps were used to collect sedimenting diatoms, the study at Lochnagar collected living diatoms directly from their habitat. It is likely that immediately prior to sampling, the diatom community was healthy and that a large proportion of the diatom frustules were comprised of hydrous silica (Si-OH groups). It is unlikely that dehydroxylation will have taken effect prior to sampling,

and consequently the potential for modification will have been at a maximum, with alteration taking place at an exponential rate post-sampling (Schmidt *et al.* 2001). The artificial substrata were removed from the loch and stored in polyethylene bags for transport to the laboratory, whereupon they were frozen before freeze drying. Possibly the $\delta^{18}O_{silica}$ values reported here were influenced by dehydroxylation under conditions of sample transportation, markedly different from those in which the silica was initially precipitated. There is therefore a need for further research, not only into the silica-water oxygen isotope fractionation during diatom growth, but also into the fractionation which takes place during opal maturation and the conditions which affect these changes.

7.5 Conclusions

Diatom silica oxygen isotope ratios ($\delta^{18}O_{silica}$) varied markedly over a monthly timescale at Lochnagar from May 2004 - November 2005. Various effects, both natural and laboratory induced, probably influenced this variability. In particular, the effects of spiking small samples is notable, and questions are raised concerning the sole use of optical microscopy for contamination screening. Unfortunately, despite best attempts to collect large volumes of diatom silica, the limited diatom productivity during certain seasons in Lochnagar led to small sample volumes, preventing a more rigorous identification of such effects. Natural effects of changing lake water $\delta^{18}O$ and water temperature do appear to

be influential, although quantification of the fractionation of oxygen isotopes between water and biogenic silica was not possible. Additional effects of water chemistry were not apparent, however a possible correlation between the taxonomic composition of the diatom assemblage and $\delta^{18}O_{silica}$ may warrant further study. In Chapters 5 and 6, it is suggested that seasonal changes in lake water conditions and diatom growth may influence the weighted average sedimentary signal. Changing seasonal patterns of diatom production can have a marked influence on sedimentary $\delta^{18}O_{silica}$, however primarily if a large ($\lambda > -0.2‰/°C$) thermal fractionation coefficient is operational. Finally, a marked difference between contemporary diatom and recent sediment $\delta^{18}O_{silica}$ raises questions regarding diagenetic effects on diatom silica oxygen isotope ratios which require quantification if the technique is to be reliably used as a palaeoclimate proxy.

Chapter 8:

Oxygen isotope ratios of diatom silica across a continental-scale climate gradient

8.1 Introduction

Previous chapters (4-7) have demonstrated that oxygen isotope ratios of precipitation ($\delta^{18}O_P$) can be largely quantified by a combination of local and regional scale meteorological variables (Chapter 4) and that the $\delta^{18}O_P$ signal is reliably transferred to lake water oxygen isotope ratios ($\delta^{18}O_L$) at Lochnagar if short term changes in water residence time are accounted for (Chapter 5). However, monthly sampling of contemporary diatoms at Lochnagar failed to demonstrate a strong, systematic response in the oxygen isotope ratios of diatom silica ($\delta^{18}O_{silica}$) to $\delta^{18}O_L$ and water temperature changes (Chapter 7). The $\delta^{18}O_{silica}$ values of contemporary diatom silica collected at Lochnagar are markedly different from the recent sediments, suggesting a degree of diagenetic modification of the $\delta^{18}O_{silica}$ signal, possibly accentuated by the sampling procedure that was carried out (Chapter 7). However, considering that in many lake systems, opal maturation and diagenesis take place in conditions similar to those of diatom growth, it is possible that a palaeo-environmental signal is

preserved within sedimentary $\delta^{18}O_{silica}$ values despite taphonomic effects (Schmidt *et al.* 1997). This chapter aims to test this hypothesis by examining $\delta^{18}O_{silica}$ values of surface sediments from lakes across a broad European climatic gradient. Surface sediments incorporate variability in growth conditions and taphonomy over a number of years and therefore offer an alternative approach to assessing the value of $\delta^{18}O_{silica}$ as a palaeoclimate proxy.

8.2 Methods

8.2.1 Acquisition of sediment material

Surface sediment was collected from a series of lakes from across Europe (Table 8.1, Figure 8.1), originally for analysis of hydrogen isotope ratios from n-alkanes (Sachse *et al.* 2004). Additional sediment material was obtained from the Environmental Change Research Centre (ECRC) sediment archive (Table 8.1, Figure 8.1). Hydrologically open-system lakes were chosen whose lake water oxygen isotope values ($\delta^{18}O_L$) are likely to represent mean annual isotopes in precipitation ($\delta^{18}O_P$). The sites cover a mean annual temperature range from -2°C (Naimakka, northern Sweden) to +13.7°C (Monticchio, southern Italy) (Table 8.1; Sachse *et al.* 2004). Sediments were collected using a gravity corer, and the

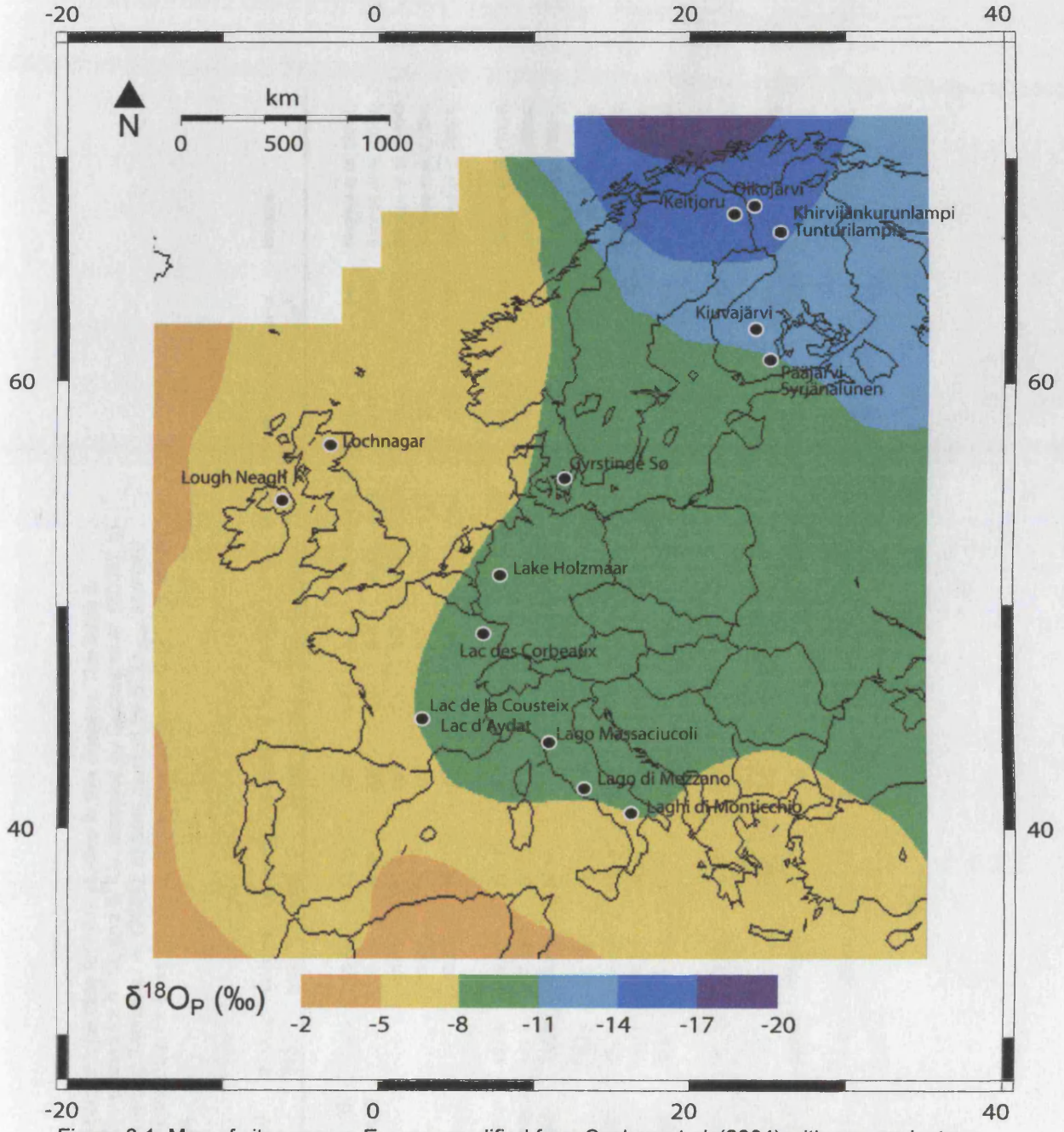

Figure 8.1: Map of sites across Europe, modified from Sachse *et al.* (2004) with oxygen isotope map curtsey of Gabriel Bowen (www.waterisotopes.org).

Table 8.1: Site details and oxygen isotope data for sites studied in this chapter. The table is divided into four groups: a) Sites studied for $\delta^{18}O_L$ and $\delta^{18}O_P$, sampled by Sachse *et al.* (2005); b) sites studied for $\delta^{18}O_{silica}$, sampled by Sachse *et al.* (2005); c) sites studied for $\delta^{18}O_{silica}$, sourced from the ECRC archive; and d) site data for Lake Chuna, published by Jones *et al.* (2004). MAAT = mean annual air temperature.

Lake name	Country	$\delta^{18}O_{silica}$ (‰)	Latitude (dec. °)	Longitude (dec. °)	Altitude m asl	$\delta^{18}O_P$ (‰)	95%CI (‰)	$\delta^{18}O_L$ (‰)	MAAT (°C)	Depth (max.) (m)	area km^2	Source
Gyrstinge So	DENMARK	-	55.55	11.70	30	-9.6	0.7	-6.4	8.6	8.2	2.640	Sachse *et al.* (2004)
Holzmaar	GERMANY	-	50.12	6.88	436	-8.8	0.4	-6.4	10.5	24.0	0.058	Sachse *et al.* (2004)
Lagi Piccolo di Monticchio	ITALY	-	40.93	15.61	685	-7.1	0.3	-4.0	13.7	36.0	0.080	Sachse *et al.* (2004)
Lago di Mezzano	ITALY	-	42.61	11.77	466	-7.0	0.7	-3.5	13.1	30.4	0.445	Sachse *et al.* (2004)
Lago di Massachiucoli	ITALY	-	43.83	10.31	18	-6.5	0.7	-6.3	14.1	2.0	7.000	Sachse *et al.* (2004)
Keitjoru	SWEDEN	+21.8	68.67	21.52	428	-14.7	1.4	-13.6	-2.0	2.0	0.010	Sachse *et al.* (2004)
Hirviiankurunlampi	FINLAND	+22.4	67.38	26.85	178	-13.2	1.1	-13.9	-0.3	4.7	0.011	Sachse *et al.* (2004)
Kiuvajärvi	FINLAND	+26.8	61.85	24.28	149	-12.3	1.0	-10.6	3.5	13.3	0.840	Sachse *et al.* (2004)
Lago Grande di Monticchio	ITALY	+34.1	40.93	15.60	674	-7.0	0.3	-0.9	13.7	36.7	0.405	Sachse *et al.* (2004)
Oikojarvi	FINLAND	+22.5	68.85	21.18	463	-14.8	1.5	-12.5	-2.0	8.4	1.500	Sachse *et al.* (2004)
Syrjanalunen	FINLAND	+25.0	61.19	25.14	156	-12.2	1.0	-12.0	3.6	8.5	0.300	Sachse *et al.* (2004)
Tunturilampi	FINLAND	+23.3	67.36	27.17	293	-13.4	1.1	-12.3	-0.3	10.7	0.360	Sachse *et al.* (2004)
Lac d'Aydat	FRANCE	+30.4	45.66	2.98	825	-8.3	0.3	-	10.5	15.0	0.600	Rioual (2002)
Lac de la Cousteix	FRANCE	+30.1	45.38	2.67	857	-8.3	0.4	-	10.5	5.0	0.009	Rioual (2002)
Lac des Corbeaux	FRANCE	+30.3	47.99	6.91	800	-9.2	0.4	-	9.4	23.0	0.09	Kreiser *et al.* (1992)
Lough Neagh	IRELAND	+30.4	54.58	-6.33	15	-8.6	0.9	-	9.1	25.0	388.000	Battarbee (1978)
Lake Chuna	RUSSIA	+21.0	67.62	32.48	475.3	-13.4	1.3	-	0.6	18.0	0.125	Jones *et al.* (2004)

upper 2 cm was sampled. This is considered to be representative of the last 5-10 years sedimentation. Preparation of sediments and analysis of oxygen isotope ratios from biogenic silica ($\delta^{18}O_{silica}$) are described in Chapter 3 (Sections 3.1.7 and 3.1.8). Initially, surface sediments from over 40 lakes were assembled and biogenic silica extraction procedures were attempted for each one. However, in most cases, standard procedures (Morley *et al.* 2004) and SPLITT fractionation (Rings *et al.* 2004; Leng and Barker 2006) failed to produced pure biogenic silica for isotope analysis. These methods rely on separating diatoms from contaminating minerals based on the different size and density of the particles (Chapter 3), however in many cases contaminating minerals are of equal size and density to diatom frustules. Extraction procedures are extremely time consuming, especially where samples are difficult to clean, and in many cases pure diatom silica can not be extracted from lake sediment (Lamb *et al.* 2006). As a consequence, only 11 samples were eventually analysed for $\delta^{18}O_{silica}$. An additional data point representing the surface sediments of Lake Chuna, Siberia (taken from Jones *et al.* 2004) was included in the analyses, since this sample was prepared identically and analysed in the same laboratory as the other material. Although small, the size of the dataset presented here is comparable with other recent studies which also attempt to evaluate developing isotope proxies using lake sediment data (e.g. Wooller *et al.* 2004; Sachse *et al.* 2004).

8.2.2 Climate, oxygen isotope and water chemistry data

Mean annual air temperature for meteorological stations close to the sampled lakes were taken from Sachse *et al.* (2004). Four sites were not sampled by Sachse *et al.* (2004), with sediment material sourced from the Environmental Change Research Centre (ECRC) archive. Climate data for these sites was obtained for the nearest meteorological station included in the European Climate Assessment Dataset (http://eca.knmi.nl/). The location of the relevant meteorological stations are as following: Lough Neagh: Belfast (81 m asl, 30 km from site); Lac d'Aydat and Lac de la Cousteix: Limoges (402 m asl, 120 km from site); Lac des Corbeaux: Basel (318 m asl, 85 km from site). Oxygen isotope ratios of precipitation ($\delta^{18}O_P$) at each site were estimated using the Online Isotopes in Precipitation Calculator (OIPC) which interpolates $\delta^{18}O_P$ between the Global Network for Isotopes in Precipitation (GNIP) monitoring stations (Bowen and Wilkinson 2002; Bowen and Revenaugh 2003) (Figure 8.1). Collection of lake water for oxygen isotope measurements were carried out during August and September 2002 (Table 8.1; Sachse *et al.* 2004). Lake water isotope data are not available for the additional sites studied (Table 8.1).

8.2.3 Data analysis

Because lake water oxygen isotope ratios were not available for all sites, oxygen isotope ratios of lake waters ($\delta^{18}O_{L\text{-}est}$) were predicted as a function of $\delta^{18}O_P$ and

estimated offset factor (δ_{OFF}), i.e. the difference between $\delta^{18}O_P$ and $\delta^{18}O_L$. δ_{OFF} was modelled empirically as a function of latitude and mean annual air temperature, using the full lake water dataset collected by Sachse *et al.* (2004) (16 data points). Using empirically derived δ_{OFF} estimates, the estimated isotope composition of lake water ($\delta^{18}O_{L\text{-}est}$) for each site was calculated as:

$$\delta^{18}O_{L\text{-}est} = \delta^{18}O_P + \delta_{OFF} \quad (1)$$

Alternative estimates for $\delta^{18}O_L$ ($\delta^{18}O_{L\text{-}Si}$) were made using surface sediment $\delta^{18}O_{silica}$ and mean annual air temperature (T) data, and a range of potential temperature coefficients (λ) based on previously published estimates (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987; Brandriss *et al.* 1998; Moschen *et al.* 2005). The fractionation factor (α) was calculated as previously (Chapter 7, Equation 3):

$$\alpha = \exp((\lambda T+\beta) / 1000) \quad (2)$$

where β is the fractionation constant (intercept). $\delta^{18}O_{L\text{-}Si}$ was estimated as:

$$\delta^{18}O_{L\text{-}Si} = ((1000 + \delta^{18}O_{silica}) / \alpha) - 1000 \quad (3)$$

Comparison of $\delta^{18}O_{L\text{-}est}$ and $\delta^{18}O_{L\text{-}Si}$ predictions, enabled a useful approach for assessing the degree to which $\delta^{18}O_{silica}$ reflects past and present climate conditions.

8.3 Results

8.3.1 Comparison of lake and meteoric waters

$\delta^{18}O$ values of the lake waters ($\delta^{18}O_L$) show a strong correlation with long term average $\delta^{18}O$ of precipitation ($\delta^{18}O_P$) (Figure 8.2) (Sachse *et al.* 2004). However, the relationship between $\delta^{18}O_L$ and $\delta^{18}O_P$ is not 1:1, with $\delta^{18}O_L$ values consistently greater than $\delta^{18}O_P$, and an increasing offset with increasing $\delta^{18}O_P$ and $\delta^{18}O_L$ (Figure 8.2). For example, where $\delta^{18}O_P \approx -10‰$, $\delta^{18}O_L \approx -6‰$; however where $\delta^{18}O_P \approx -6.5‰$, $\delta^{18}O_L \approx -0‰$ (Figure 8.2). The sites with the largest offset are those located in southern France and Italy, whereas those with the smallest offset are located in arctic Sweden and Finland.

The $\delta^{18}O$ offset for each site (δ_{OFF}, calculated as $\delta^{18}O_P - \delta^{18}O_L$) is significantly correlated ($p = <0.05$) with both mean annual air temperature and latitude (Figures 8.3 (a) and (b)). Most likely due to increasing evaporation effects at warmer, more southerly latitudes (Gat 1995). Regression between δ_{OFF} and air temperature and latitude yields the following linear models:

$$\delta_{OFF} = -0.3005T - 0.994 \quad (4)$$

$$\delta_{OFF} = 0.1763L - 12.7423 \quad (5)$$

Where T = mean annual air temperature (°C), and L = latitude (°N).

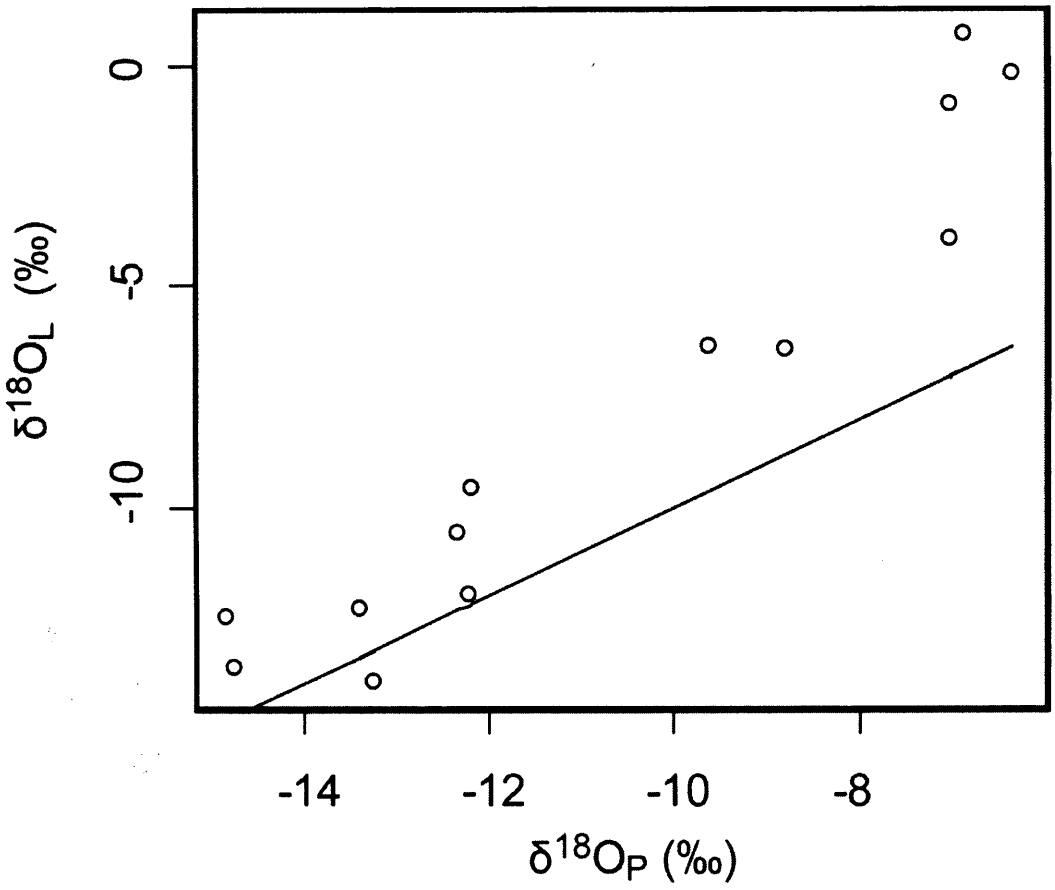

Figure 8.2: Comparison of $\delta^{18}O$ for precipitation and lake waters for all available sites (re-drawn from Sachse *et al.* 2005). Solid line = 1:1 line.

8.3.2 Oxygen isotopes in biogenic silica

Surface sediment $\delta^{18}O_{silica}$ values range from +21.0‰ at Lake Chuna (Russia) to +34.1‰ at Lago Grande di Monticchio (Italy). There is a marked trend of increasing values with decreasing latitude, and significant correlation

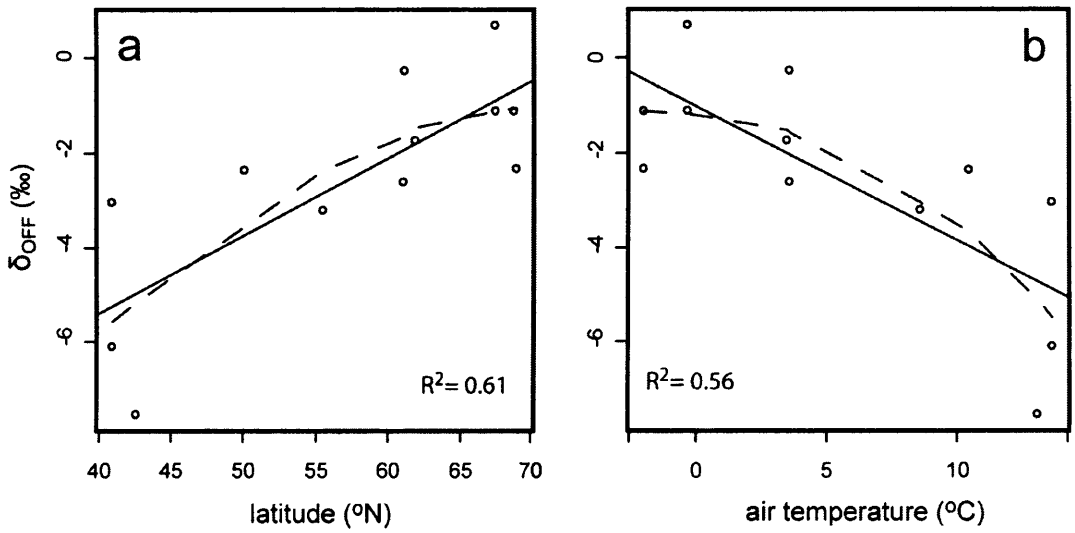

Figure 8.3: $\delta^{18}O_P - \delta^{18}O_L$ offset against (a) latitude and (b) mean annual air temperature. Dashed line = lowess smoothed response, solid line = linear regression line. Both linear models are significant ($p = <0.05$).

with latitude, mean annual air temperature (Figure 8.4 (a) and (b)) and $\delta^{18}O_P$ (Figure 8.5). The relationship between $\delta^{18}O_{silica}$ and $\delta^{18}O_P$ is strongly linear, however the regression slope is 0.62, rather than 1 - indicating that fractionation must have modified the oxygen isotope signal at some point between $\delta^{18}O_P$ and $\delta^{18}O_{silica}$.

Where lake water isotope composition estimates ($\delta^{18}O_{L\text{-}est}$; Equation 1) are substituted for $\delta^{18}O_P$ (Figure 8.6), the slope of the regression line ≈ 1, suggesting that hydrological effects account for the majority of the difference between $\delta^{18}O_{silica}$ and $\delta^{18}O_P$, which are separated by a constant fractionation factor of ~35.5‰. For comparison, recent Lochnagar sediment $\delta^{18}O_{silica}$ and the range of contemporary $\delta^{18}O_{silica}$ values from Lochnagar (Chapter 7; Morley et al. 2004) are

plotted (against Lochnagar 2004-2005 mean annual $\delta^{18}O_L$) (Figure 8.6) . Lochnagar

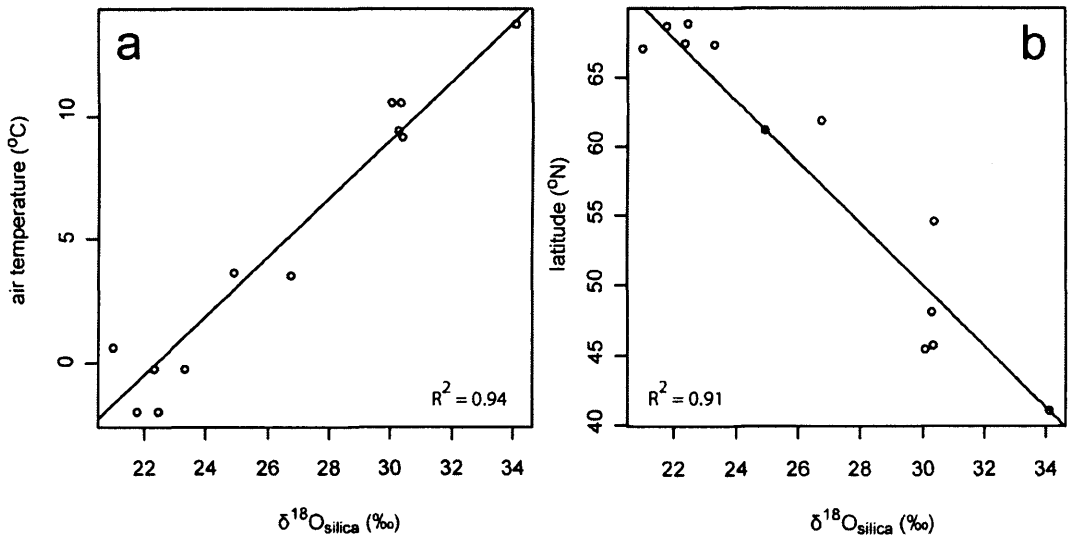

Figure 8.4: $\delta^{18}O_{silica}$ from lake surface sediments against (a) mean annual air temperature and (b) latitude. Solid line = linear regression line.

sediment $\delta^{18}O_{silica}$ values plot close to the European regression line, however contemporary $\delta^{18}O_{silica}$ values are offset with $\delta^{18}O_{silica}$ values anomalously high compared with the overall dataset (Figure 8.6).

Figures 8.7a and 8.7b compare $\delta^{18}O_{L\text{-}Si}$ with $\delta^{18}O_P$ and $\delta^{18}O_{L\text{-}est}$. The predictions suggest that raw $\delta^{18}O_P$ values do not represent the formation conditions of the diatom silica: even when potential variations in the temperature fractionation coefficient are taken into account, $\delta^{18}O_{L\text{-}Si}$ values markedly differ from $\delta^{18}O_P$ (Figure 8.7a), similar to the difference between observed $\delta^{18}O_L$ and $\delta^{18}O_P$ (Figure 8.2). $\delta^{18}O_{L\text{-}est}$ values, which take into account the offset between $\delta^{18}O_L$ and $\delta^{18}O_P$, compare more favourably with $\delta^{18}O_{L\text{-}Si}$ (Figure 8.7b). In this case, increasing the

temperature coefficient, leads to a decrease in the slope of observed vs. predicted, away from 1. $\delta^{18}O_{L\text{-}Si}$ estimates based on a low temperature coefficient, or none at all (i.e λ <0.1), are more closely associated with $\delta^{18}O_{L\text{-}est}$.

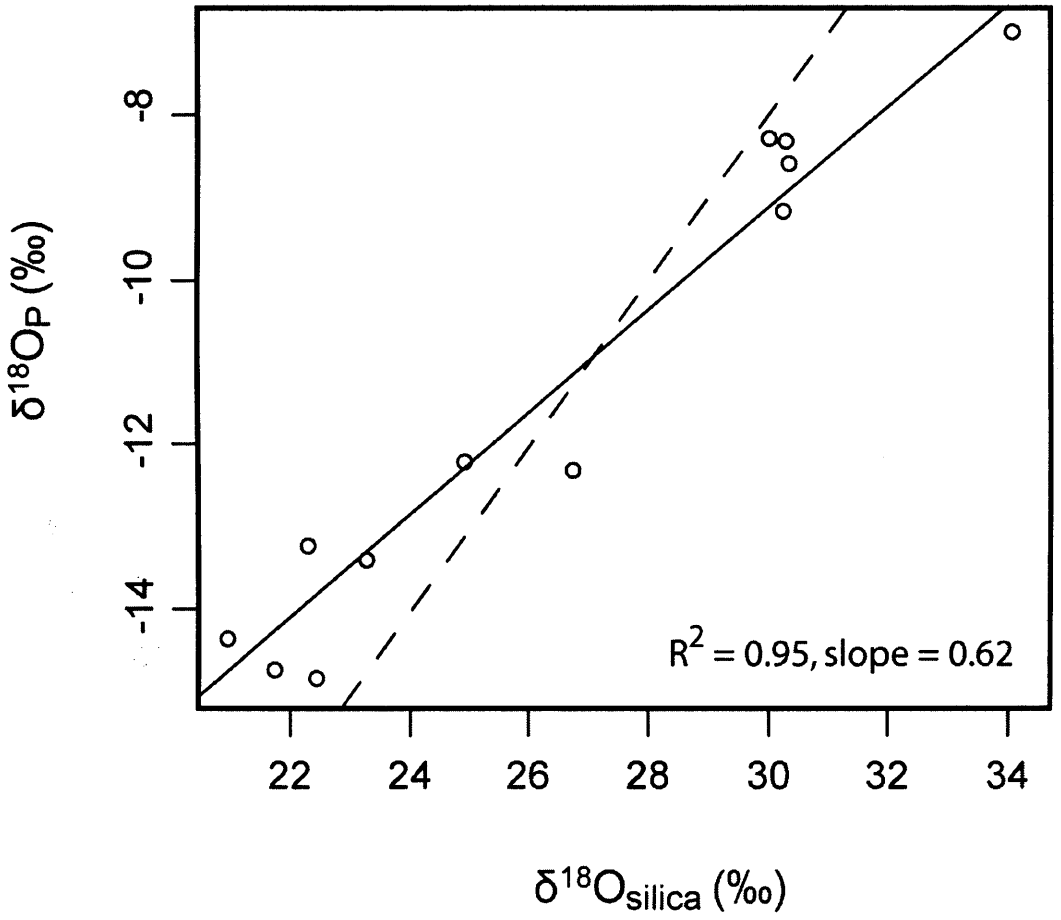

Figure 8.5: $\delta^{18}O_{silica}$ from lake surface sediments against $\delta^{18}O$ of precipitation. Solid line = linear regression line; dashed line = constant fractionation line (i.e. λ = 0, β = +35‰ (arbitrary)).

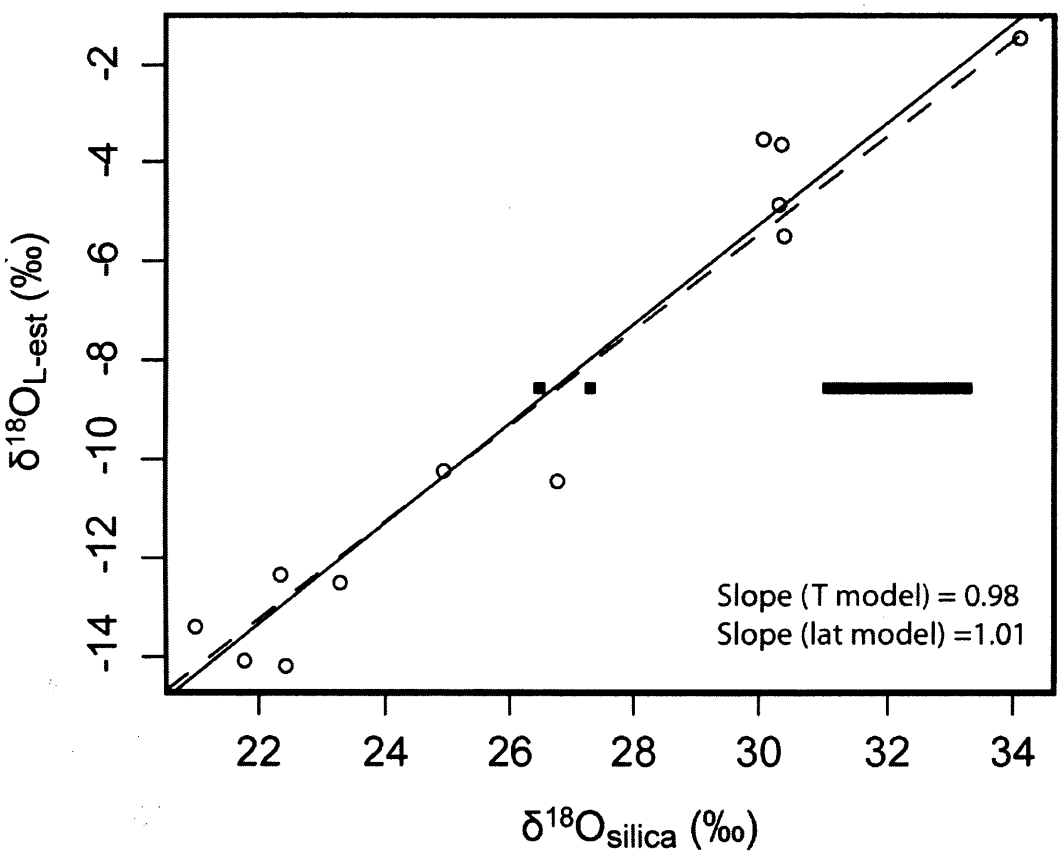

Figure 8.6: $\delta^{18}O_{silica}$ of lake surface sediments against $\delta^{18}O_L$ estimated using temperature model ($\delta^{18}O_{L\text{-}est}$: Equations 1 and 4; dashed line) and latitude model ($\delta^{18}O_{L\text{-}est}$: Equations 1 and 5; solid line). Solid black squares represent recent lake sediment $\delta^{18}O_{silica}$ values (Morley et al. 2004) against mean $\delta^{18}O_L$ for Lochnagar (2004-2005) (Chapter 5). Solid black bar represents range of contemporary $\delta^{18}O_{silica}$ values measured at Lochnagar over 2004 and 2005 (Chapter 7).

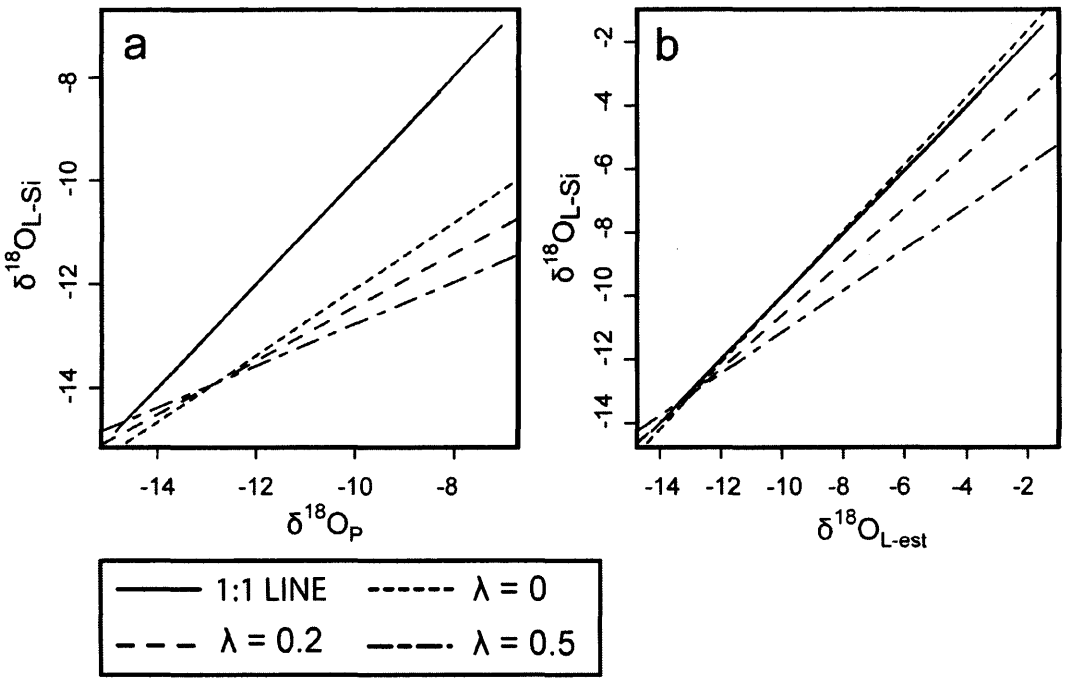

Figure 8.7: (a) Observed $\delta^{18}O_P$ and (b) estimated $\delta^{18}O_L$ ($\delta^{18}O_{L\text{-}est}$: based on Equations 1 and 5) against predicted $\delta^{18}O$ of formation waters from diatom silica ($\delta^{18}O_{L\text{-}Si}$).

8.4 Discussion

8.4.1 Isotope composition of formation waters

Analysis of previously published lake water oxygen isotope data (Sachse *et al.* 2004) allows a preliminary assessment of the relationship between the oxygen isotope composition of lake and rain waters on the European continental scale, enabling empirical models to be derived to compensate for the lack of water isotope data for some sites. Study sites were selected on the criteria that the lakes were hydrologically open with a long lake-catchment water residence time sufficient for long term mixing and smoothing of lake water oxygen isotope

values. In theory, therefore, the isotope composition of lake water ($\delta^{18}O_L$) should reflect a time-averaged signal of the $\delta^{18}O$ of precipitation ($\delta^{18}O_P$). The offset between $\delta^{18}O_P$ and $\delta^{18}O_L$, and the significant correlation of this offset with both latitude and temperature is strongly indicative of the effects of evaporation on $\delta^{18}O_L$ at the warmer, southernmost sites. It is therefore necessary to account for the potential effects of evaporation when judging the formation conditions for sediment biogenic silica. There are likely to be considerable uncertainties regarding estimates made from the derived empirical models (Equations 4 and 5), primarily due to the inherent seasonality of lake systems (Chapter 5), the importance of lake morphology on evaporation (Gat 1995) and the effect of differing oxygen isotope composition of atmospheric water vapour between sites (Yurtsever and Gat 1981). Lake water samples were taken at the height of summer, where evaporation is likely to have been at a maximum, and $\delta^{18}O_L$ values probably do not reflect annual average conditions (Sachse *et al.* 2004). In addition, diatom growth is also heavily seasonal, usually reaching maxima in spring and autumn overturn periods (e.g. Raubitschek *et al.* 1999; Chapter 6). However, in some respects the approach taken here to predict lake water isotope ratios may be beneficial, since long term averages smooth out much of the short term variability.

8.4.2 Oxygen isotopes in diatom silica

Comparing contemporary and sedimentary $\delta^{18}O_{silica}$ values from Lochnagar within a broader continental scale framework further supports the interpretation that the contemporary $\delta^{18}O_{silica}$ values measured from Lochnagar were affected by a diagenetic process. The apparent fit of Lochnagar sediment $\delta^{18}O_{silica}$ with the other European surface sediment data strongly suggests that diatom silica $\delta^{18}O$ signals are accrued not only during diatom growth and silica assimilation, but also following diatom death and decay, via opal maturation during silica sedimentation.

The dataset of surface sediment $\delta^{18}O_{silica}$ values across Europe suggest that even if $\delta^{18}O_{silica}$ values are fixed during both silica formation and sedimentation, their sedimentary values do preserve a record of regional climate. Strong correlations between $\delta^{18}O_{silica}$, air temperature and latitude reflect the co-correlation of those parameters with $\delta^{18}O_P$ which in turn is the major control over geographical variability in $\delta^{18}O_L$. By accounting for the effects of evaporation on $\delta^{18}O_L$, the data suggest that $\delta^{18}O_{silica}$ is related to $\delta^{18}O_L$ via an almost constant fractionation of 35.5‰. However, a lack of precision concerning the temperature and oxygen isotope composition of formation lake waters means that a temperature effect over isotope fractionation can not be ruled out. The data suggest, however, that the influence of temperature on the fractionation is relatively weak – supporting recent calculations of $\lambda = -0.2$ ‰/°C (Brandriss *et al.*

1998; Moschen *et al.* 2005) over earlier estimates of $\lambda = -0.5$ ‰/°C (Labeyrie 1974; Juillet-Leclerc and Labeyrie 1987; Matheney and Knauth 1989). The range of contemporary values analysed from Lochnagar suggests a slightly greater temperature coefficient (Chapter 7, Section 7.4.2), however it is uncertain whether these data are affected by modification during sampling. Some degree of the difference between fractionation coefficients observed by previous researchers may be due to the fact that, until relatively recently (Schmidt *et al.* 1997), such diagenetic effects over $\delta^{18}O_{silica}$ data have been given relatively little consideration. Brandriss *et al.* (1998) and Moschen *et al.* (2005) present convincing evidence that, for contemporary diatom silica, a temperature fractionation of –0.2‰/°C takes place. However as Schmidt *et al.* (1997; 2001) and Moschen *et al.* (2006) demonstrate, sedimentation of diatom frustules may lead to a modification of the $\delta^{18}O_{silica}$ signal fixed during valve formation. It is possible that diagenetic processes may counteract initial temperature effects over isotope fractionation that act during diatom valve formation - effectively reducing the fractionation coefficient for sedimentary diatom silica.

In this study, lake water conditions for diatom growth and silica sedimentation were very poorly constrained – in particular $\delta^{18}O_L$ was estimated very coarsely from interpolated evaporation effects which are doubtless subject to error. In addition, the assumption that lake water temperature is equivalent to or related directly to mean annual air temperature may be inaccurate for all sites, particularly since some sites are further from the meteorological station than

others (Table 8.1). Further research should include more detailed contemporary lake surveys and controlled experiments using laboratory cultures in order to properly assess the fractionation of oxygen isotopes between water and diatom silica.

8.5 Conclusion

Recent research has demonstrated a marked dissimilarity between contemporary and sediment $\delta^{18}O_{silica}$ values which are explained by opal maturation effects during sedimentation (Schmidt *et al.* 1997; 2001; Moschen *et al.* 2006). $\delta^{18}O_{silica}$ analysis of contemporary diatom samples from Lochnagar support this hypothesis, with $\delta^{18}O_{silica}$ values markedly different from recent sediments (Chapter 7). In addition, the relationship between $\delta^{18}O_{silica}$, $\delta^{18}O_L$ and water temperature over the two years monitored at Lochnagar do not conform to any previous model for equilibrium silica-water fractionation, possibly indicating isotope fractionation post-sampling (Chapter 7). $\delta^{18}O_{silica}$ values of lake surface sediments ameliorate some of these sampling issues by undergoing opal maturation and potential isotope re-equilibration within the lake water. Therefore, there remains potential that the $\delta^{18}O_{silica}$ record of lake sediments is quantifiably related to climate change.

Analysis of $\delta^{18}O_{silica}$ from surface sediments of lakes across Europe appear to demonstrate a linear relationship with climate. Recent sediments from Lochnagar

fall within a marked trend for increasing $\delta^{18}O_{silica}$ with decreasing latitude, reflecting the continental scale gradient of oxygen isotope ratios in precipitation and lake waters. It would appear, therefore, that oxygen isotope ratios of sedimentary diatom silica do record regional scale climate variability, despite probable taphonomic effects. The effect of temperature on $\delta^{18}O_{silica}$ values appears to be less than previous estimates for contemporary diatoms (Brandriss *et al.* 1998; Moschen *et al.* 2005). It is possible that this relates to diagenetic effects, however imprecise controls over lake conditions during diatom silica formation and sedimentation prevent a more accurate assessment. The dataset does highlight the potential of using oxygen isotope ratios of biogenic silica as a proxy for past environmental change, however further work is required to precisely quantify the isotope fractionations during diatom growth and subsequent degradation.

Chapter 9:

Synthesis: interpreting past climate from oxygen isotope ratios of sedimentary diatom silica

9.1 Introduction

Previous chapters (Chapters 4-8) have explored the processes which combine to determine the oxygen isotope record preserved in the sediment biogenic silica of Lochnagar. This chapter aims to collate this information and discuss the implications of studying the contemporary system for palaeoclimate research.

9.1.1 Synthesis of climate-lake interactions at Lochnagar

9.1.1.1 Precipitation water

Compared with many lake systems, the climate-lake interface at Lochnagar is relatively simple. The oxygen isotope composition of precipitation, on a monthly timescale, is largely driven by changes in air temperature. Precipitation amount

also appears to exert a degree of control over $\delta^{18}O_P$ at Lochnagar, however the dataset is too small to identify a statistically significant relationship (Chapter 4). Elsewhere in the British Isles, air mass circulation patterns, in particular the strength of the westerly flow, can also influence $\delta^{18}O_P$ (Chapter 4).

9.1.1.2 Lake water

The oxygen isotope composition of lake water ($\delta^{18}O_L$) at Lochnagar predominantly reflects the oxygen isotope composition of precipitation ($\delta^{18}O_P$), mediated by the amount of precipitation (P) reaching the lake, through changes in throughflow rate and residence time (Chapter 5). There are negligible effects of evaporation on lake water $\delta^{18}O$ and there is no influence of glacial meltwater or large scale groundwater flow – experienced by many similar lakes in arctic or alpine environments (e.g. Krabbenhoft *et al.* 1990; Shemesh *et al.* 2001; Rosqvist *et al.* 2004). Seasonal lake stratification does affect short-term $\delta^{18}O_L$ patterns, however the overall lake water oxygen isotope composition is modelled reasonably well using a basic mass balance model consisting of simply $\delta^{18}O_P$, P and the lake and catchment dimensions (Chapter 5).

9.1.1.3 Diatom ecological effects and silica-water fractionation

Within the contemporary lake there is one dominant diatom habitat – the epilithon (Flower *et al.* 2007). Diatom production is expected to extend to the limits of the photic zone (approx. 8 m deep), and hence there is probably a moderate degree of variation in water temperature (T_w) and $\delta^{18}O_L$ which influence the isotope composition of diatom silica ($\delta^{18}O_{silica}$) produced within the lake at a specific point in time. The maximum T_w range between 1.5 and 9 m is 4.5°C during periods of lake water stratification (D. Monteith, unpublished data). A vertical profile of $\delta^{18}O_L$ has never been measured, however water throughout the photic zone is usually well mixed (Chapter 1) and the mean temperature range between 1.5 and 9 m is a negligible 0.1°C. Therefore heterogeneity in $\delta^{18}O_L$ and T_w conditions are unlikely to have a major impact on time-averaged sediment $\delta^{18}O_{silica}$ values. This is unlike some large lake systems, where within-lake heterogeneity, in particular vertical stratification, can markedly influence the sediment $\delta^{18}O$ signal (e.g. von Grafenstein *et al.* 1999).

9.1.1.4 Impact on palaeoclimate interpretation

$\delta^{18}O_L$, T_w and consequently $\delta^{18}O_{silica}$ vary seasonally, along with marked seasonality in diatom standing crop (Chapters 6 and 7). These effects are likely

to have an influence on the sedimentary weighted average $\delta^{18}O_{silica}$ signal, in particular if a large thermal effect over silica-water fractionation (i.e. ~ –0.5‰/°C) is eventually demonstrated (e.g. Shemesh *et al.* 1992) (Chapter 7). In addition, changes to the seasonal pattern of diatom standing crop can lead to further changes to mean sediment $\delta^{18}O_{silica}$ values (Chapter 7, Figure 7.10). However, assuming a constant pattern of seasonal diatom growth, the Lochnagar sediment $\delta^{18}O_{silica}$ record can generally be interpreted as a response to changing $\delta^{18}O_P$ (i.e. T_{air} and P) and water temperature (T_w, a function of T_{air}).

Due to the dynamic nature of the Lochnagar ecosystem, the relatively small size of the lake and catchment and the resulting short water residence time, each component of the system is best explained over a short term (monthly) timescale. Interpretation in terms of annual average climate forcing will inevitably lead to a reduction in the precision of palaeoclimate reconstructions – most notably in explaining $\delta^{18}O_P$, which is heavily influenced by the timing of rainfall occurrences throughout the year (Chapter 4). In addition, although most isotope variability at Lochnagar can be explained as a function of either P or T, these factors are influential in a number of processes – for example P is a major factor influencing $\delta^{18}O_P$ (Chapter 4), it affects the weighting of $\delta^{18}O_L$ by the precipitation of particular seasons and determines the residence time of lake water and hence the seasonal responsiveness of $\delta^{18}O_L$ to changes in $\delta^{18}O_P$ (Chapter 5). T_{air} has a positive relationship with $\delta^{18}O_P$ (Chapter 4), but T_w is inversely related to the silica-water oxygen isotope fractionation during diatom silica formation (Chapters

7 and 8). Consequently, although the climate forcing on isotope hydrology at Lochnagar is relatively simple compared with many lake systems, palaeoclimate interpretation of the sediment $\delta^{18}O_{silica}$ record is complex.

9.1.2 Approaches to interpreting $\delta^{18}O_{silica}$ records

9.1.2.1 Single climatic variable

Lacustrine $\delta^{18}O_{silica}$ records are no different from the majority of palaeo-environmental proxies in their inherent multifactorial nature. The traditional approach to interpreting most palaeodata is to identify the primary control and interpret the sediment record as a singular response to that control. For example, at Lochnagar we could assume that $\delta^{18}O_P$ is the primary control over $\delta^{18}O_{silica}$. There is evidence to suggest that air temperature affects $\delta^{18}O_P$, and therefore the $\delta^{18}O_{silica}$ record can be interpreted as a proxy for past air temperature (e.g. Eicher and Siegenthaler 1976; Hu and Shemesh 2003). This approach has considerable limitations for a number of reasons. Most importantly, all additional variables that may influence the signal are ignored, and the assumption is required that the balance between controlling factors over $\delta^{18}O_P$, $\delta^{18}O_L$ and $\delta^{18}O_{silica}$ remained constant over time. When considering just one climate variable, this assumption is difficult to accept.

In a number of palaeolimnological studies, the interpretation of the sediment record varies down core (e.g. Jones *et al.* 2004; Rosqvist *et al.* 2004) due to inexplicable changes in the $\delta^{18}O_{silica}$ values. Researchers are often forced to alter their interpretation strategy for different sections of the sediment profile, where changes in the contemporary primary control (i.e. air temperature in this case) do not feasibly explain the observed pattern. Therefore, whilst offering valuable qualitative observations on past climate and environmental change, this approach often means the abandonment of rigorous quantitative interpretation.

9.1.2.2 Linked multiple proxies

A second approach, common in palaeoceanography (Duplessy *et al.* 1970; Shackleton 1987; Maslin and Swann 2005) and gaining increasing interest in palaeolimnology (Anderson *et al.* 1996; Hammarlund *et al.* 2002; 2003), is to combine multiple proxy records in order to isolate individual variables. For example using marine sediments, independent estimates of sea surface salinity can be made by subtracting the effects of water temperature (derived using the U^k_{37} index or Ca/Mg ratios) and global ice volume (benthic foraminifer $\delta^{18}O$) from the planktonic foraminifer $\delta^{18}O$ record (Duplessy *et al.* 1970). For a Holocene lake sediment profile in southern Sweden, Hammarlund *et al.* (2002) compared palaeoclimate records derived by authigenic calcite $\delta^{18}O$ ($\delta^{18}O_{calcite}$) and pollen-inferred air temperature (Hammarlund *et al.* 2002). Throughout much of the profile, air temperature changes are closely related to $\delta^{18}O_{calcite}$, except for the

early Holocene, where there is a marked divergence between the two which Hammarlund *et al.* (2002) interpret as reflecting changing atmospheric circulation. At Lochnagar, following the scenario outlined above, an independent temperature proxy would allow the temperature effects over $\delta^{18}O_P$ and $\delta^{18}O_{silica}$ to be removed. This would produce a record of temperature-independent $\delta^{18}O_P$, possibly reflecting past precipitation amount. However, such an approach can still be problematic (Benson and Paillet 2002). In particular, a significant simplification of the system is required, and certain potentially influential variables may be ignored. Considering the large diversity of lacustrine systems, making generalisations concerning the relative influence of various climate parameters can be difficult. In addition, the approach of combining proxy datasets is sensitive to the cumulative error in the various reconstructions, whereby an error in predicting temperature will have an influence on the eventual precipitation reconstruction. Most importantly, however, the majority of palaeolimnological climate proxies are poorly calibrated (Benson and Paillet 2002). Attempts have been made using biological indicators (chironomids, diatoms, cladocera, terrestrial pollen and macrofossils) (Walker *et al.* 1991; Lotter *et al.* 1997; Rosen *et al.* 2000; Bigler and Hall 2003; Heiri *et al.* 2003; Heiri and Lotter 2005) however these proxies also suffer from multiple controls and non-linear responses to climate (Chapter 1). Emerging organic biomarker techniques – such as TEX_{86} and U^k_{37} – have demonstrated some applicability to lake records (Zink *et al.* 2001; Powers *et al.* 2004; 2005; Chu *et al.* 2005; Liu *et al.* 2006), but to date these techniques remain unproven. There is some potential for combining

$\delta^{18}O$ records from different sediment compounds whose oxygen isotope ratios respond differently to temperature – e.g. biogenic silica and calcium carbonates. However, attempts at combining $\delta^{18}O$ records have so far proved unfruitful, possibly due to within-lake differences in the spatial and seasonal production of diatoms and carbonates (Leng *et al.* 2001a; Lamb *et al.* 2005). Fundamentally, the number of lines of evidence that can be extracted from the sediment are invariably outweighed by the variety of environmental variables which may have influenced them.

9.1.2.3 Forward models

A third approach to using and interpreting palaeoclimate records from sediment (or other) archives is to incorporate the sediment-forming processes within climate models. The climate model is used to hypothesise the effects of particular climate changes on the sediment record which are tested against observed data (i.e. the measured profile). This approach is known as forward modelling and has been used regularly in studies of polar ice core records (Joussaume *et al.* 1984; Jouzel *et al.* 1994; 2000), tree rings (e.g. White *et al.* 1994; Roden *et al.* 2000) and marine sediments (Schmidt 1999; Schmidt and Mulitza 2002; Le Grande *et al.* 2006; Ridgwell 2006). Forward modelling has been used with lake sediment oxygen isotope records to investigate the influence of various controlling factors (Benson and Paillet 2002; Jones *et al.* 2005). Climate models are a logical means of synthesising palaeoclimate data. Coupling palaeodata with climate

models enables issues such as variable resolution, response and sensitivity between archives to be dealt with quantitatively, offering an effective tool for assessing the effects of global climate change on localised marine, polar and terrestrial records. For example, Le Grande *et al.* (2006) used a coupled General Circulation Model to predict changes in polar $\delta^{18}O_P$, aerosol deposition and wetland methane emissions in response to a hypothetical meltwater pulse in the North Atlantic Ocean. By quantitatively matching model predictions with palaeoclimate data, other aspects of the model simulation – namely the effect on North Atlantic circulation, could be assessed (Le Grande *et al.* 2006). The most important aspect of forward modelling is ensuring reliable quantitative models of the contemporary system. For Lochnagar, constraints can be placed to varying degrees of precision and accuracy on all aspects of the climate-sediment interface. Consequently, Lochnagar is an ideal site for modelling the sediment record. Modelling the processes which combine to produce a palaeoclimate archive also enables an extrapolation of the contemporary system beyond the limits of the monitoring record, allowing an assessment of the potential effects of long term climate change on the sediment record (e.g. Ricketts and Johnson 1996; Benson and Paillet 2002; Jones *et al.* 2005).

This chapter aims to synthesise the various controls over the sediment $\delta^{18}O_{silica}$ record for Lochnagar by modelling the sediment profile deposited during the recent instrumental period (1800-2000). This is compared with $\delta^{18}O_{silica}$ results from a short sediment core, NAG19 (Chapter 1). A number of important factors

remain to be addressed – most notably the acquisition of a reliable $\delta^{18}O_{silica}$ profile. This and other outstanding issues are discussed.

9.2 Methods

9.2.1 Deriving a $\delta^{18}O_{silica}$ record for Lochnagar

A short sediment core, NAG19 was collected, analysed for dry density, loss-on-ignition and potassium (K) concentration and dated using ^{210}Pb and spheroidal carbonaceous particles as part of a previous research project (Yang 2000). Subsequently, the core was analysed for $\delta^{18}O_{silica}$ by Leng *et al.* (2001b: unpublished conference abstract). Because the potential effects of contaminating silica were given less consideration at the time, no diatom cleaning procedure was implemented. Consequently, the $\delta^{18}O_{silica}$ profile is highly correlated with the concentration of minerogenic matter – here indicated by potassium (K) concentration (Figures 9.1 and 9.2). Attempts were made as part of this project to isolate pure biogenic silica from the remaining NAG19 samples for further analyses, however these proved unsuccessful – primarily due to the small residual sample volumes. Due to time constraints, collection, dating and stratigraphic analysis of a new core from Lochnagar was considered beyond the remit of this PhD research. An alternative record of diatom $\delta^{18}O_{silica}$ change, possibly independent of contamination effects, was derived by calculation of the

residuals of linear regression between $\delta^{18}O_{silica}$ and K (Figure 9.2). $\delta^{18}O_{silica}$ change ($\Delta\delta^{18}O_{silica}$) was therefore estimated as:

$$\Delta\delta^{18}O_{silica} = \delta^{18}O_T - \delta_K \quad (1)$$

where $\delta^{18}O_T$ is the oxygen isotope composition of the total silica sample and δ_K is the linear effect of K on $\delta^{18}O_T$ derived from a regression between $\delta^{18}O_T$ and K

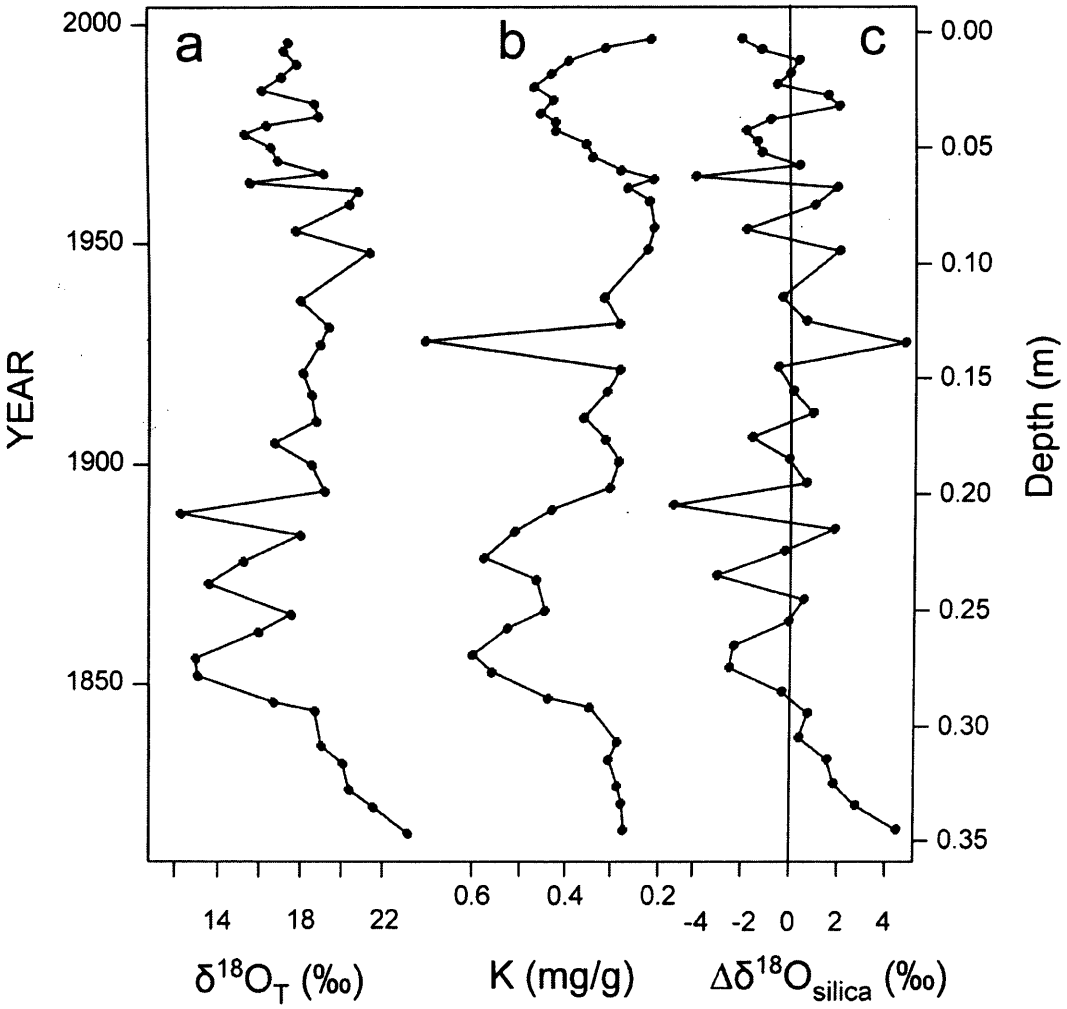

Figure 9.1: a) $\delta^{18}O_T$ (‰) – oxygen isotope ratios for total silica sample, core NAG19, Lochnagar; b) K concentration per inorganic (including biogenic) sediment weight (mg/g); c) estimated $\Delta\delta^{18}O_{silica}$ with the effect of mineral contamination (indicated by K) removed from $\delta^{18}O_T$.

(mg/g) (Figure 9.2), expressed as a proportion of the inorganic sediment mass (M_I), calculated as:

$$M_I = DD_T * (1 - f_{LOI}) \quad (2)$$

Where DD_T is the dry density of the total sample and f_{LOI} is the organic fraction of the total sample lost on ignition at 550°C. The removal of the contamination signal via the influence of K is shown in Figure 9.1.

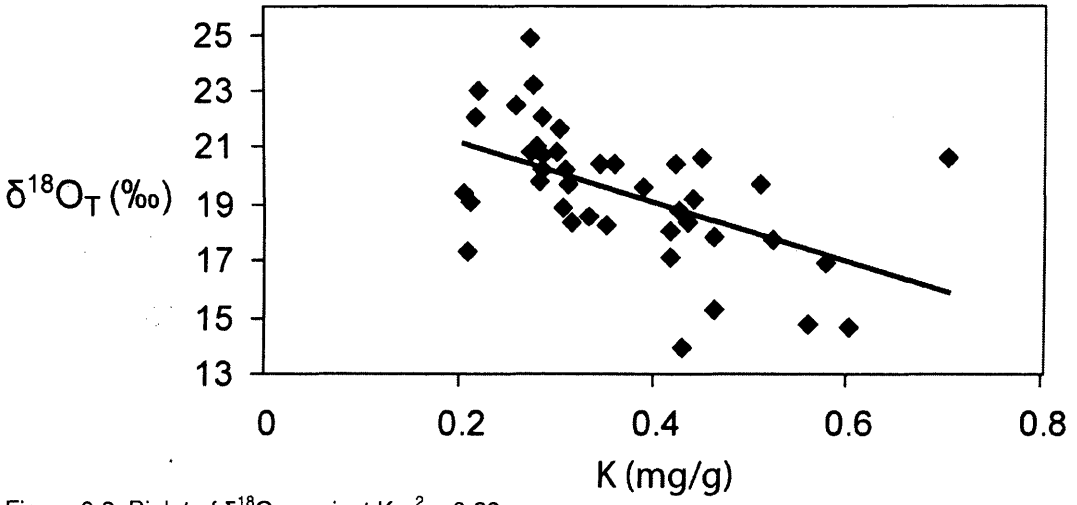

Figure 9.2: Biplot of $\delta^{18}O_T$ against K. $r^2 = 0.29$.

9.2.2 Modelling the Lochnagar $\delta^{18}O_{silica}$ sediment profile

9.2.2.1 Climate data

For comparison with observed data and $\Delta\delta^{18}O_{silica}$ estimates from K residuals, a modelled $\delta^{18}O_{silica}$ profile was also generated for Lochnagar using instrumental

climate data. The data used were monthly mean air temperature for central England (Central England Temperature, CET) (Manley 1953; Manley 1974; Parker *et al.* 1992) and monthly mean precipitation for Braemar (Chapter 2, Figure 2.1). Air temperature and precipitation amount at Lochnagar were estimated by linear extrapolation from the CET and Braemar precipitation datasets respectively (Figure 9.3). Monthly mean air temperature at Lochnagar is strongly correlated with CET (Figure 9.3a), whilst Braemar precipitation amount gives a reasonable fit with Lochnagar values (Figure 9.3b). The Balmoral climate dataset, which was collected closer to Lochnagar and used in Chapter 5, could not be used in these analyses due to the short length of the record.

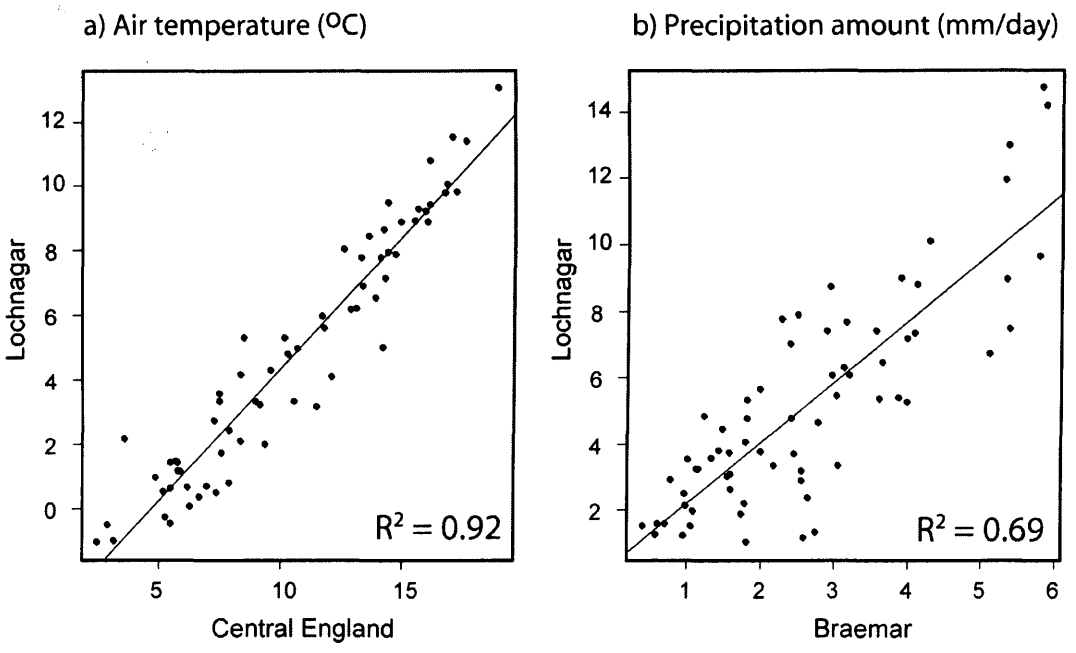

Figure 9.3: Model timeseries inputs (air temperature, precipitation and westerly flow) and modeled outputs ($\delta^{18}O_P$, $\delta^{18}O_L$ and $\delta^{18}O_{silica}$) for Lochnagar.

9.2.2.2 $\delta^{18}O_P$ predictions

Monthly $\delta^{18}O_P$ for Lochnagar was predicted using the empirical model established in Chapter 4:

$$\delta^{18}O_P = 0.23T_{air} - 73.46 \quad (3)$$

where T_{air} = air temperature (^oK). Monthly $\delta^{18}O_L$ was estimated using a simple mass balance model (Chapter 5) following Gat (Gat 1995):

$$\Delta\delta^{18}O_{L(t)} = (IN/V).(\delta^{18}O_{P(t)} - \delta^{18}O_{L(t-1)}) \quad (4)$$

where $\Delta\delta^{18}O_L$ is change in the isotope composition ($\delta^{18}O$) of lake water and t denotes the specific month in question. Therefore, $\delta^{18}O_{L(t-1)}$ is the $\delta^{18}O_L$ of the previous month. Initial $\delta^{18}O_L$ (for January 1880) was estimated as the mean monthly $\delta^{18}O_P$ estimated for preceding year (1879). No evidence of drift due to model equilibration can be detected. V is lake water volume and IN is the total input volume, calculated as a function of precipitation amount, catchment and lake surface area and an estimated runoff coefficient (Chapter 5, Section 5.2.2).

The $\delta^{18}O_{silica}$ value of monthly sedimenting diatom silica was estimated as a function of the isotope composition of water ($\delta^{18}O_L$) and water temperature (T_w) (assumed to equal air temperature, T_{air}). Due to a lack of certainty concerning the

exact temperature effects on silica-water isotope fractionation, three fractionation factors were used:

$$\alpha_{0} = 35.5 \quad (5)$$

$$\alpha_{-0.2} = (-0.2 * T_w) + 35.5 \quad (6)$$

$$\alpha_{-0.5} = (-0.5 * T_w) + 35.5 \quad (7)$$

where α is the silica-water fractionation factor and the subscript (i.e. 0, –0.2 or –0.5) denotes the temperature fractionation coefficient (λ). Equation 5 (α_{0}) describes a constant fractionation, close to that observed between surface sediment $\delta^{18}O_{silica}$ and $\delta^{18}O_L$ for European surface sediments (Chapter 8, Figure 8.7b) and therefore possibly incorporates the potential effects of diagenetic modification. $\delta^{18}O_{silica}$ was estimated as:

$$\delta^{18}O_{silica} = ((\exp(\alpha_{\lambda} / 1000)) * (1000 + \delta^{18}O_L)) - 1000 \quad (8)$$

Sediment $\delta^{18}O_{silica}$ values were calculated as the mean of monthly $\delta^{18}O_{silica}$, weighted by the monthly diatom flux, for the period of time represented by the corresponding NAG19 core sample. Diatom flux was estimated as:

$$D = (0.2401*m^6) - (7.8191*m^5) + (71.657*m^4) + (101.16*m^3)$$

$$- (4439.7*m^2) + (18482*m) - 14368 \quad (9)$$

where m = month of the year (i.e. January = 1, March = 3 etc..). Negative values of D were replaced by zero, assuming no productivity during January and February, when the lake is usually covered in ice (Chapter 6, Figure 6.16).

9.3 Results

9.3.1 Sedimentary $\delta^{18}O_{silica}$ profile for Lochnagar

Changes in down-core $\delta^{18}O_{silica}$ ($\Delta\delta^{18}O_{silica}$) independent of contamination effects, were calculated as a function of measured $\delta^{18}O_{silica}$ ($\delta^{18}O_T$) and the concentration of K in the inorganic (including biogenic silica) portion of the sediment. Essentially this approach is same as the linear mass balance approach used by previous researchers (Morley *et al.* 2005; Thorpe 2006; Lamb *et al.* 2007), except that the $\delta^{18}O_{silica}$ of an end-member contamination sample, and the specific volume of diatom silica and contaminant were not estimated. Instead, it is assumed that the volumetric ratio between diatom and mineral silica is proportional to the K concentration in the inorganic sediment component. Measured $\delta^{18}O_{silica}$ values are correlated with K ($r^2 = 0.29$, significant to $p < 0.05$; Figure 9.2) suggesting that a large portion of the down-core variance is explained by contamination effects. The residual variance ($\Delta\delta^{18}O_{silica}$), having removed the

effect of K on the $\delta^{18}O_{silica}$ signal, is markedly reduced (standard deviation = 1.68‰) and is assumed to reflect changes in the $\delta^{18}O_{silica}$ of diatom frustules. Using this approach, absolute $\delta^{18}O_{silica}$ values can not be estimated, therefore isotope values are expressed as changes (Δ). Maximum values occur at the bottom of the core (~AD 1820), with additional positive changes in ~AD 1880 and ~ AD 1990. Notable negative changes occur in AD 1890 and AD 1965. There is no marked trend in the data, except for the decline in values between AD 1820 and 1860 (Figure 9.1c).

This approach assumes that (a) the relative proportion of K in contaminating minerogenic matter is constant (i.e. that the clay and silt types are constant); and (b) the $\delta^{18}O_{silica}$ of contaminating minerogenic matter is constant. Both assumptions are difficult to justify, since changes in weathering patterns will cause changes in the composition of minerogenic flux to the sediment. At Lochnagar, however, there is one dominant bedrock type (Gibson 2007), and assuming that a negligible amount of mineral matter is removed from the catchment, the mineral composition of the sediment should predominantly reflect that of the surrounding granite geology. It is unclear how changing weathering effects may have altered the $\delta^{18}O_{silica}$ and elemental composition of contaminating minerogenic matter. Assumption (b) is consistent with that made by Morley *et al.* (2005) and Thorpe (2006). Lamb *et al.* (2007) partially account for the issue by analysing pure contaminant samples (from volcanic tephra horizons) at intervals throughout the core. The approach also assumes that

diatom silica and organic matter contain negligible K. Although little has been published concerning the K content of diatom silica, it is generally believed to be low. Peakall (1993) measured between 0.6-0.12% K in diatoms in the surface sediments of Loch Leven, Scotland, whilst Lamb *et al.* (2007) found ~0.58% in diatomite material from Lake Tilo, Ethiopia which they believe to reflect minor contamination.

9.3.2 Modelled $\delta^{18}O_{silica}$ profile for Lochnagar

The signal cascade from air temperature and precipitation amount through $\delta^{18}O_P$ and $\delta^{18}O_L$ is illustrated for Lochnagar in Figure 9.4. The well documented long term air temperature trend is characterised by a very gradual warming, over marked seasonal variability. Precipitation amount demonstrates a weaker long term trend and is characterised by short term periods of heavy rainfall. However, precipitation over the period 1930 - 1970 at Braemar is notably less than between 1970 - 2000. Past changes in $\delta^{18}O_P$ were modelled as the sole function of air temperature (Equation 3). Estimated $\delta^{18}O_P$ values fluctuate between –11‰ and –8‰, within the range of contemporary precipitation at Lochnagar (Chapter 4). Changes in $\delta^{18}O_L$ are marked, although the range of variability is lower than $\delta^{18}O_P$ (~±0.4‰). Because $\delta^{18}O_P$ is fairly stable over the long term, changes in $\delta^{18}O_L$ respond predominantly to precipitation amount, specifically by weighting of short term, seasonal $\delta^{18}O_P$. For example, the heavy precipitation during 1980

places extra weight on winter $\delta^{18}O_P$ values, resulting in a time-lagged decrease in $\delta^{18}O_L$ (Figure 9.4).

Modelled $\delta^{18}O_{silica}$ values fluctuate moderately throughout the time series, however marked seasonal changes dominate the pattern and the decadal-scale variability seen in $\delta^{18}O_L$ is less evident. $\delta^{18}O_{silica}$ predictions in Figure 9.4 are based on a temperature coefficient (λ) of –0.2‰/°C. Increasing or decreasing the predicted temperature coefficient leads to marked effects on the seasonal amplitude of modelled $\delta^{18}O_{silica}$ (Figure 9.5). For example, the range of variability is < ±0.4‰ where $\lambda = 0$, ~ ±1‰ where $\lambda = -0.2$ and ~±3‰ where $\lambda = -0.5$ (Figure 9.5).

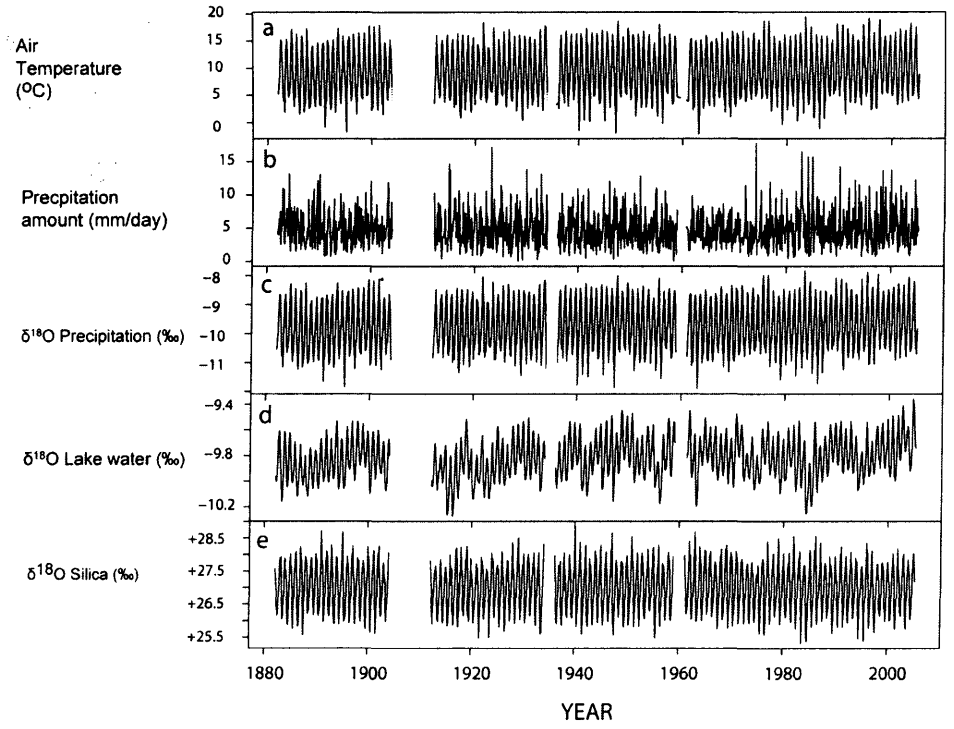

Figure 9.4: Breakdown of components of the $\delta^{18}O_{silica}$ model using monthly instrumental air temperature (Central England) and precipitation (Braemar). $\delta^{18}O_P$ and $\delta^{18}O_L$ calculated using models developed for Lochnagar (Chapters 4 and 5). $\delta^{18}O_{silica}$ calculations represent λ = –0.2‰/°C.

Calculation of weighted means of modelled monthly $\delta^{18}O_{silica}$ values, weighted by monthly diatom abundance for time-slices equivalent to the temporal resolution of NAG19, leads to a marked smoothing of the $\delta^{18}O_{silica}$ signal (Figure 9.6b). The three modelled profiles demonstrate similar patterns, except for some slight differences, in particular between the estimates for $\lambda = 0$ and $\lambda = -0.5$. The values predicted using $\lambda = -0.5$ fluctuate most markedly throughout the series, however most of the variability throughout the modelled profile is within the minimum analytical error (~ 0.3‰) for $\delta^{18}O_{silica}$ analysis.

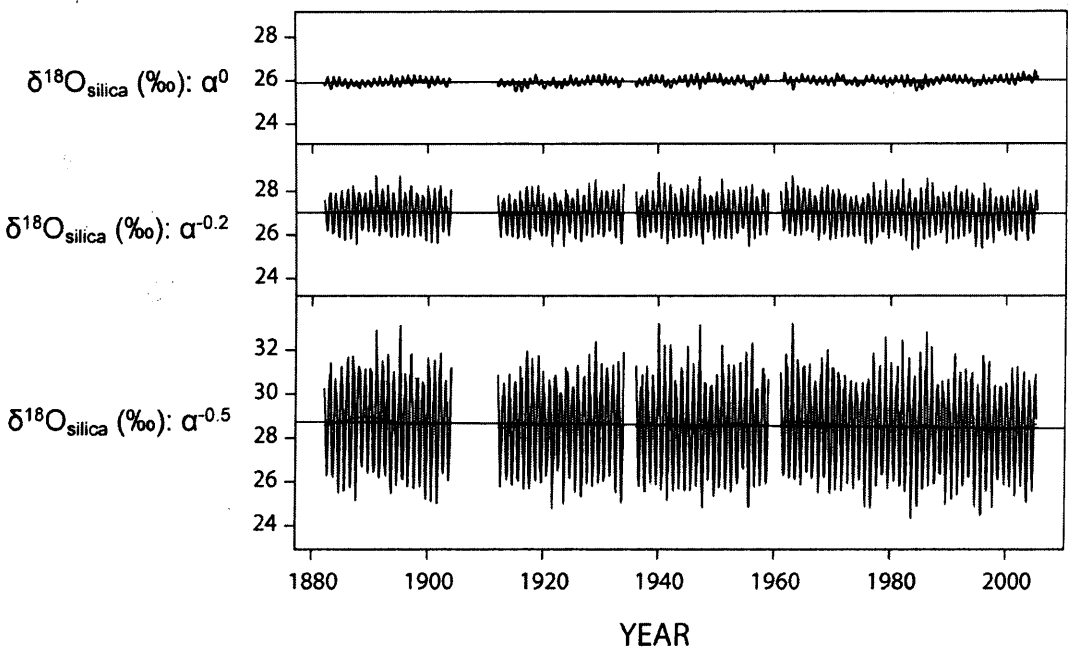

Figure 9.5: Modelled monthly $\delta^{18}O_{silica}$ according to three hypothetical temperature fractionation coefficients $\lambda = 0‰/°C$ (α^0), $\lambda = -0.2‰/°C$ ($\alpha^{-0.2}$) and $\lambda = -0.5‰/°C$ ($\alpha^{-0.5}$). Gaps in the dataset are due to gaps in the Braemar meteorological record.

9.3.3 Comparing modelled and stratigraphic $\delta^{18}O_{silica}$

Comparison between the modelled $\delta^{18}O_{silica}$ profiles for Lochnagar, based on potential silica-water temperature coefficients of 0, –0.2 and –0.5‰/°C (Figure 9.6b) and the NAG19 $\Delta\delta^{18}O_{silica}$ profile (Figure 9.6a) suggests a tentative correlation between $\Delta\delta^{18}O_{silica}$ and modelled values using –0.5‰/°C, with notable peaks and troughs roughly coinciding (indicated in Figure 9.6). However, this correlation is tenuous and the range of NAG19 $\Delta\delta^{18}O_{silica}$ values (±4‰) greatly outweigh that of the modelled values.

9.3.4 Comparing modelled $\delta^{18}O_{silica}$ with climate variables

Although the modelled $\delta^{18}O_{silica}$ record for Lochnagar is derived entirely from instrumental meteorological data, the relationship between modelled $\delta^{18}O_{silica}$ and climate is likely to be complex, due to interactions between the various input variables and the temporal smoothing associated with a sediment core. It is therefore beneficial to investigate the correlation between modelled sedimentary $\delta^{18}O_{silica}$ and the major climate variables we may wish to reconstruct. Figures 9.7 and 9.8 compare modelled $\delta^{18}O_{silica}$ values for Lochnagar with mean air temperature, precipitation amount and amount weighted $\delta^{18}O_P$, derived for representative time-slices equivalent to the core resolution. Other than a clear

association between air temperature and $\delta^{18}O_{silica}$, under a scenario where $\lambda = -0.5$, a correlation between modelled $\delta^{18}O_{silica}$ and the major climate variables is

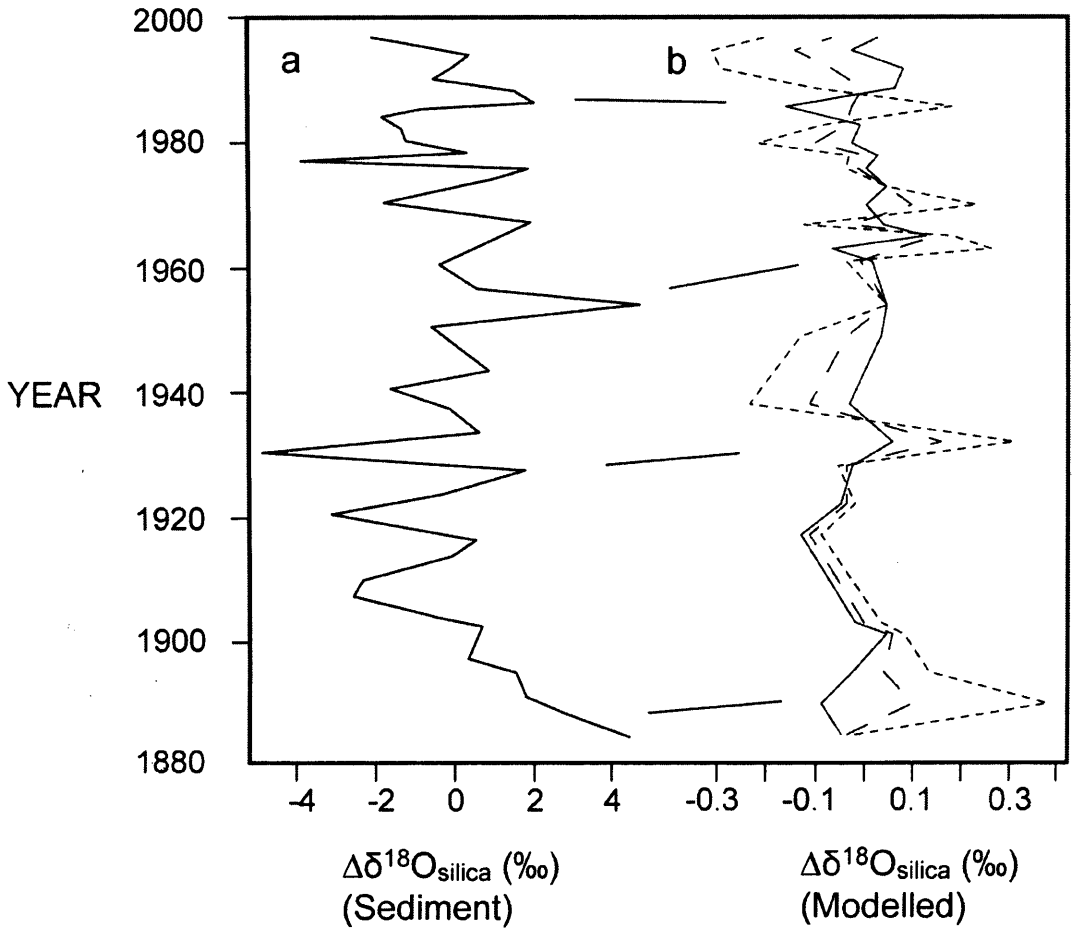

Figure 9.6: Comparison of estimated change (Δ) in $\delta^{18}O_{silica}$ derived from (a) the residual variance of sediment $\delta^{18}O_{silica}$ measurements with the effects of contamination as indicated by K concentration removed; and (b) Modelled $\delta^{18}O_{silica}$ profiles based on instrumental climate data using silica-water temperature fractionation coefficients (λ) of 0 (solid line), –0.2 (dashed line) and –0.5 (dotted line). Straight lines between the plots highlight potential tie points between the two profiles (discussed in text).

not obvious when comparing the timeseries (Figure 9.7). However, significant negative correlations do exist between air temperature and $\delta^{18}O_{silica}$ using $\lambda = -0.2$ and $\lambda = -0.5$ models (Figure 9.8), albeit a weak correlation (r^2 =

0.28) where $\lambda = -0.2$. Estimated $\delta^{18}O_{silica}$ using $\lambda = 0$ is significantly positively correlated with amount weighted $\delta^{18}O_P$ and to a lesser extent, negatively correlated with precipitation amount (Figure 9.8). $\delta^{18}O_{silica}$ estimated using $\lambda = -0.2$ does not demonstrate a strong correlation with any of the three climate indices (Figure 9.8).

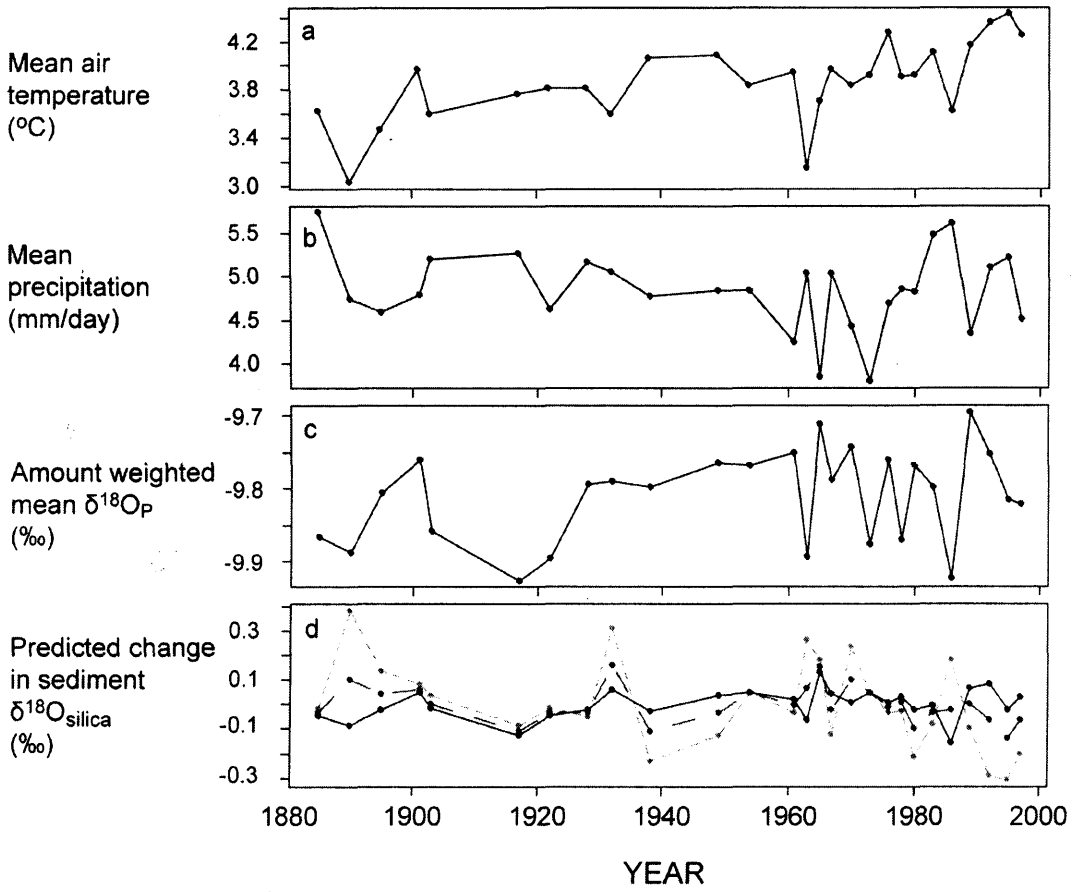

Figure 9.7: Modelled $\delta^{18}O_{silica}$ sediment profiles (d) compared with mean annual air temperature (a), mean precipitation (b) and mean calculated $\delta^{18}O_P$, weighted by precipitation amount (c), each calculated as the mean corresponding to the time slices dictated by the chronological resolution of the NAG19 core. In (d), $\lambda = 0$ (solid line), $\lambda = -0.2$ (dashed line) and $\lambda = -0.5$ (dotted line).

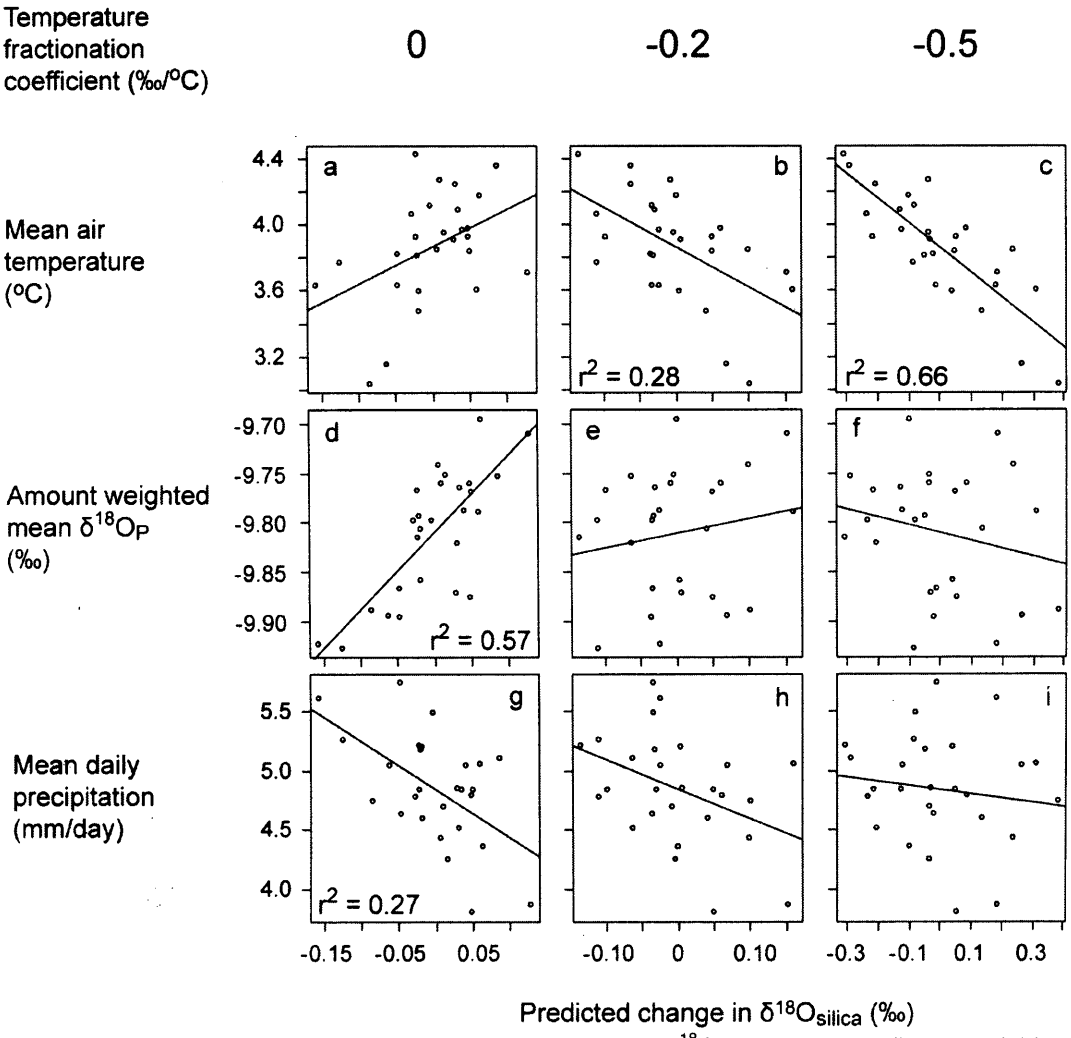

Figure 9.8: Correlation bi-plots between modelled sediment $\delta^{18}O_{silica}$ and mean climate variables for corresponding time slices. Solid lines represent linear best fits.

9.4 Discussion

In order to investigate the potential of forward modelling lake sediment $\delta^{18}O_{silica}$ records for incorporation with climate models, a 200 year sediment record for Lochnagar was modelled and compared with both a previously collected $\delta^{18}O_{silica}$ profile and mean values for the primary climate indices (air temperature, precipitation amount and $\delta^{18}O_P$). The exercise highlights a number of shortcomings related to both forward modelling $\delta^{18}O_{silica}$ and obtaining reliable $\delta^{18}O_{silica}$ data from sediment cores.

9.4.1 Consideration of potential modelling errors

Modelled $\delta^{18}O_{silica}$ records were based on air temperature from central England (Manley 1953; 1974) and precipitation data for Braemar, extrapolated to estimate conditions at Lochnagar. Ideally, local climate records collected at Lochnagar would be used, however such data do not exist, and strong correlations between Lochnagar, Braemar and central England climate suggest that the extrapolation of climate data is not a major factor in introducing error to the modelled sediment profile.

Another potential source of error lies in the extension of the empirical $\delta^{18}O_P$ model (Equation 3) over long timescales. Although this model predicts $\delta^{18}O_P$ reasonably well over the monitored period (Chapter 4), the length of the

monitoring record at Lochnagar is relatively short and it is uncertain how long term changes in climate are manifest in $\delta^{18}O_P$ (Chapter 4).

$\delta^{18}O_L$ values were predicted as a function of changing $\delta^{18}O_P$ and precipitation amount following the model derived in Chapter 5. This assumes negligible effects of evaporation, snow influx and stratification changes. Although such changes may have occurred over the recent past, the conservative changes in air temperature over this period (Figure 9.4) suggest that changes to the lake isotope hydrology are unlikely to have varied sufficiently to affect the model output. However, over longer timescales the effects of lake water evaporation and changing catchment vegetation cover may have been more influential. Evaporation effects can be modelled (e.g. Gibson *et al.* 2001) but ideally require validation against an analogous contemporary system. Changing catchment vegetation cover may have altered the proportion of rainfall reaching the lake via runoff – and hence will affect the catchment water residence time. Although this is difficult to quantify, analysing the pollen and macrofossil record of terrestrial vegetation (e.g. Dalton *et al.* 2005) can identify periods where changing catchment dynamics might have been influential. Changes in lake water stratification and ice cover appear to exert a lesser control over $\delta^{18}O_L$ at Lochnagar but could play an increasingly important role with changing climate (Chapter 5). Therefore, potential improvements to the model could include aspects of lake water physics and ice cover dynamics (e.g. Benson and Paillet 2002).

$\delta^{18}O_{silica}$ was modelled as a function of $\delta^{18}O_L$ and water temperature – assumed to equal air temperature. Recent monitoring of Lochnagar water temperature (Chapter 1) reveals a close similarity between air and water temperatures over the annual cycle. If necessary, a more rigorous approach would be to use the polynomial mixing model of Kettle *et al.* (2004) in order to derive a water temperature-depth profile from which to calculate $\delta^{18}O_{silica}$ values. With regards the fractionation of oxygen isotopes between water and diatom silica, no account was taken here for potential diagenetic effects since these processes, should they occur, are yet to be quantified. However, modelled $\delta^{18}O_{silica}$ following the reduced temperature effect observed for surface sediments across Europe (Chapter 8) may partially account for taphonomic processes such as diagenesis and opal maturation.

The assumption of a constant seasonal distribution of diatom abundance is likely to be a major limiting factor. Changing patterns of diatom monthly abundance can lead to marked alterations in the sediment $\delta^{18}O_{silica}$ signal (Chapter 6) and it is unlikely that the patterns observed over 2004 and 2005 have been constant with time, in particular in response to changing climate conditions. A more appropriate approach to modelling diatom flux would be the incorporation of a dynamic algal model, such as PROTECH (Reynolds 1997; Elliot *et al.* 2006). However, to date, such models have yet to be applied to periphyton, which account for the majority of diatoms at Lochnagar. A further issue, not addressed by this research is one of spatial patterns in diatom productivity. Diatom growth

takes place throughout the photic zone of Lochnagar, and hence at varying temperatures. For most of the year, waters are well mixed and therefore the difference in water temperature and $\delta^{18}O_L$ between locations within the lake is unlikely to be significant. However, at certain periods this may have had an effect – particularly when lake waters were stratified, at which point diatom silica produced beneath the thermocline will have different $\delta^{18}O_{silica}$ values to that produced in the surface waters. At present, however, there is no information concerning the distribution of diatom biomass with depth at Lochnagar.

9.4.2 Consideration of the modelled and sediment $\delta^{18}O_{silica}$ profiles for Lochnagar

The ultimate test of the modelled $\delta^{18}O_{silica}$ sediment profile for Lochnagar is it's correlation with measured values from a sediment core. In the absence of an uncontaminated sediment $\delta^{18}O_{silica}$ record to date, modelled $\delta^{18}O_{silica}$ was compared with estimated $\delta^{18}O_{silica}$ changes derived as the residuals between measured $\delta^{18}O_{silica}$ values and the potassium (K) concentration, used as a tracer for mineral contamination. The two profiles do not correlate – with particular disagreement concerning the range of variability throughout the record. Considering the likely limitations of using K to separate out the contamination signal, it is more realistic to infer that the more reliable of the two records is the modelled profile.

The modelled $\delta^{18}O_{silica}$ record, irrespective of it's correlation with analysed sediment values, offers a useful tool for evaluating current understanding concerning the potential climate controls over an uncontaminated $\delta^{18}O_{silica}$ record. The effects of changes in temperature and precipitation amount are manifest in the sediment record through a number of processes – affecting the isotope composition of precipitation, the residence time and mixing of precipitation within lake water and the fractionation of oxygen isotopes between water and diatom silica. Therefore, it might be expected that the modelled $\delta^{18}O_{silica}$ profile will correlate with changes in temperature, precipitation or calculated $\delta^{18}O_P$, from which it is derived. However, due to the complex interactions between these variables, the eventual correlation with $\delta^{18}O_{silica}$ is generally weak, depending on the temperature fractionation coefficient used in the model (Figure 9.8). For example, $\delta^{18}O_{silica}$, assuming no temperature fractionation ($\lambda = 0$) is essentially a function of changing $\delta^{18}O_L$ and therefore $\delta^{18}O_P$. $\delta^{18}O_P$ is derived solely from air temperature data, however modelled $\delta^{18}O_{silica}$ demonstrates no significant correlation with air temperature (Figure 9.8a). Instead, $\delta^{18}O_{silica}$ ($\lambda = 0$) is significantly correlated with precipitation amount due to the effects of changing amount of winter rainfall leading to biased lake water isotope ratios (Figures 9.4b and d). Sediment $\delta^{18}O_{silica}$ values modelled assuming a large temperature dependent fractionation ($\lambda = -0.5$) are dominated by an inverse correlation with temperature (Figure 9.8c) and no correlation with $\delta^{18}O_P$ or precipitation amount. Predictions made assuming a lesser temperature effect ($\lambda = -0.2$) are also inversely correlated with temperature, however the

relationship is much weaker. This is of particular importance considering the λ = –0.2 fractionation coefficient is the most likely coefficient, according to recent published calculations (Brandriss *et al.* 1998; Moschen *et al.* 2005). If a λ = –0.2 fractionation coefficient is subsequently proven, climate changes of the magnitude of the past century in Scotland will have left very little clear evidence in the Lochnagar $\delta^{18}O_{silica}$ record without a consideration of the total combination of processes from which it is derived.

9.5 Conclusions

Forward modelling of $\delta^{18}O_{silica}$ records in lake sediments offers great potential in hypothesis-based palaeoclimate science. However, a disparity between modelled and sedimentary evidence for the instrumental period highlights considerable uncertainty both within our ability to model sediment records, and to extract reliable $\delta^{18}O_{silica}$ data from sediments. Consequently, further attention to develop both theoretical understanding and practical application is required in order to reliably use $\delta^{18}O_{silica}$ as a palaeoclimate tool.

Unfortunately, there is little correlation between modelled $\delta^{18}O_{silica}$ and the $\Delta\delta^{18}O_{silica}$ profile estimated from the residuals of a $\delta^{18}O_T$~K regression. The $\Delta\delta^{18}O_{silica}$ signal has a much greater amplitude of variability than modelled estimates and contrasts with the relatively conservative climate changes that have occurred over the recent past. Consequently, it would appear that the

sediment $\Delta\delta^{18}O_{silica}$ record is the less reliable of the two. Probably, the lack of correlation between the two lines of evidence is due to a failure of one of the assumptions in using K concentration to remove the effects of contamination on $\delta^{18}O_{silica}$. For example, changes in the flux of quartz grains to the sediment will have had no effect on K concentration but marked effects on $\delta^{18}O_T$. A more appropriate approach would be to consider the entire minerogenic composition of the sediment in order to more precisely remove the effects of contamination by mass balance (e.g. Lamb *et al.* 2007).

The assumptions necessary for both constructing a lake sediment $\delta^{18}O_{silica}$ record and interpreting it in terms of palaeoclimate change are identical to those required for forward modelling the lake sediment record. By using a modelling approach, however, the limitations in the assumptions are more transparent and hence a more rigorous approach to interpretation can be achieved. The majority of assumptions made in modelling the $\delta^{18}O_{silica}$ profile for Lochnagar are reasonably acceptable. However, the modelled profiles, with $\delta^{18}O_{silica}$ ranges generally less than the 0.3‰ analytical error, suggest that the sediment record is probably largely insensitive to changes of the magnitude of the past century. Furthermore, the profiles do not consistently correlate with the climate predictors (air temperature and $\delta^{18}O_P$) from which they were initially derived. This is particularly significant where an isotope fractionation temperature coefficient of –0.2‰/°C is used. In this case, the contrasting effect of temperature over $\delta^{18}O_P$ silica-water isotope fractionation leads to a weakening of the eventual signal.

Establishing the true fractionation coefficient is of prime importance, since the correlation between $\delta^{18}O_{silica}$ and climate varies markedly according to the coefficient used. Where the temperature effect is low ($\lambda = 0$), $\delta^{18}O_{silica}$ generally reflects $\delta^{18}O_P$ (but not temperature). Where the temperature effect is large ($\lambda = -0.5$), $\delta^{18}O_{silica}$ can more reliably be interpreted as past temperature.

Considering the complexity in the transmission of climate change through to the $\delta^{18}O_{silica}$ record at Lochnagar, the use of process based models, such as that described in this chapter, appears to be the most appropriate approach to interpreting palaeoclimate change from the sediment record. In particular, this enables the testing of climate change hypotheses using the sediment profile for validation (e.g. Le Grande *et al.* 2006; Ridgwell 2006). However, in order for this to be achieved, reliable sediment records are required and a greater understanding of the isotope fractionation between diatom silica and water is necessary.

Chapter 10: Conclusion

The aim of this thesis was to explore the cascade of processes that combine to produce oxygen isotope signals in lake sediments, with particular focus on the oxygen isotope ratios of diatom silica. The research was primarily carried out through a case study of Lochnagar, a remote upland lake in eastern Scotland. The general aim of the investigation was to derive a quantitative understanding of the climate-lake-biology system and develop a methodology for more rigorous interpretation of lake sediment palaeoclimate records. In particular, the following objectives were addressed:

10.1 The relationship between oxygen isotopes in contemporary precipitation in the British Isles and contemporary climate.

This study combined new data for bi-weekly $\delta^{18}O$ in precipitation ($\delta^{18}O_P$) at Lochnagar, Scotland, with monthly datasets from Valentia, Wallingford and Keyworth to assess the significance of meteorological variables on $\delta^{18}O_P$ in the British Isles. Chapter 4 presents multivariate statistical analyses of local meteorological data (air temperature and precipitation amount) combined with regional scale air flow indices (the Jenkinson dataset: Jenkinson and Collinson 1977; Jones *et al.* 1993) in order to derive empirical models for $\delta^{18}O_P$. At all four sites, temperature was found to be the primary factor explaining most of the variance in $\delta^{18}O_P$, however precipitation amount and the velocity of westerly air

circulation also play an important role in some circumstances. Interestingly, the relative effect of each parameter varied according to site, for example $\delta^{18}O_P$ at the maritime site (Valentia) was more susceptible to changes in circulation effects than $\delta^{18}O_P$ at the inland and high altitude Lochnagar. Due to the uneven and irregular distribution of precipitation throughout the year, $\delta^{18}O_P$ records are best interpreted as a cumulative response to short-term meteorological processes rather than a simple average of annual-scale climate change.

10.2 The relationship between oxygen isotopes in precipitation and Lochnagar lake water ($\delta^{18}O_L$).

Chapter 5 presents bi-weekly $\delta^{18}O$ measurements of lake inflow, outflow and precipitation waters in order to characterise the isotope hydrology of Lochnagar. Lochnagar has a cool-temperate/montane climate, with a small catchment, and evaporation of surface waters therefore has a minimal effect on $\delta^{18}O_L$. Effects of water residence time, stratification and seasonal ice formation, however, combine to add complexity to the signal. Of particular importance is the effect of precipitation amount on the seasonal amplitude of $\delta^{18}O_L$ changes, and consequently the oxygen isotope composition of formation waters during diatom growth. The oxygen isotope composition of lake waters at Lochnagar was modelled using a simple mass balance equation (Gat 1995) dependent on the amount of water input relative to lake volume, and the isotope composition of

precipitation ($\delta^{18}O_P$). Using this model, a better appreciation of $\delta^{18}O_L$ responses to climate change can be achieved.

10.3 The effect of the seasonality in diatom growth on oxygen isotope ratios of sediment diatom silica

The cell density and relative abundance of diatom species was studied on a monthly basis during ice-free periods over 17 months at Lochnagar. Diatom productivity was highly seasonal – with highest production during the early spring and late autumn. Therefore, oxygen isotope ratios of sediment diatom silica at Lochnagar are likely to be weighted towards spring and autumn lake conditions. Seasonal changes in diatom growth respond to a combination of changing ice cover, lake mixing and nutrient availability. Despite marked changes in diatom abundance throughout the year, there was no clear pattern in diatom species composition - possibly due to persistent instability within the ecosystem.

10.4 The relationship between oxygen isotope ratios in contemporary diatom silica and formation waters.

This was initially investigated through monthly collection of living diatoms on large-surface artificial substrata suspended within Lochnagar. Artificial substrata were deployed in the lake and replaced on a monthly basis over a 17 month period. On retrieval, diatoms were scrubbed off, cleaned of organic and mineral

contaminants and analysed for oxygen isotopes ($\delta^{18}O_{silica}$). Due to the marked seasonality in diatom productivity at Lochnagar, a rigorous assessment of diatom isotope fractionation was not possible, since a large proportion of samples yielded diatom silica volumes insufficient for isotope analyses. The magnitude of $\delta^{18}O_{diatom}$ changes over the annual cycle suggests a thermal effect over isotope fractionation, in the region of –0.3‰/°C. However, the weighted mean $\delta^{18}O_{diatom}$ of modern samples at Lochnagar (~30‰) is markedly higher than that of recent surface sediments (~25‰), reported by Morley *et al.* (2004). Although recent environmental changes may have had some effect, it is possible that this offset relates to opal maturation during sedimentation (Schmidt *et al.* 2001; Moschen *et al.* 2006).

In order to evaluate the relationship between climate and sedimentary $\delta^{18}O_{silica}$, thus accounting for taphonomic processes, $\delta^{18}O_{silica}$ was analysed from a set of surface sediments from lakes across a large European climate gradient. Samples were collected via other research projects from lakes situated between arctic Sweden and central Italy for comparison with local climate and isotope data. Surface sediment $\delta^{18}O_{silica}$ demonstrated a clear association with estimated $\delta^{18}O_L$, derived from $\delta^{18}O_P$, however the effect of temperature on $\delta^{18}O_{silica}$ (<– 0.1‰/°C) appeared to be weaker than previous estimates (Brandriss *et al.* 1998; Moschen *et al.* 2005). Due to poor constraints over formation conditions however, further research is required to determine the significance of these findings. Lake sediments from Lochnagar conform to the general trend across

Europe, lending further support to the apparently anomalous data from contemporary material which is possibly related to diagenetic effects.

10.5 Method development

An important aspect of this research was to further the development of analytical and preparation methods for analysis of $\delta^{18}O_{silica}$. In particular, experiments were carried out to test the effects of organic removal treatment on the integrity of oxygen isotope measurements from diatom silica (Chapter 3, Section 3.3.1.; Tyler *et al.* 2007). Several methods were tested for effectiveness of organic matter removal and their effects on $\delta^{18}O_{diatom}$ values. Hot digestion in hydrogen peroxide and ignition in air at 550°C were the most effective at removing organic matter whilst having minimal effect on $\delta^{18}O_{diatom}$ (Tyler *et al.* 2007).

10.6 General implications for palaeoclimate research

The research presented in this thesis demonstrates that lake waters and sediments are highly responsive to climate variability, and that such responses are predictable, enabling accurate palaeoclimate reconstruction. Competing effects of primary controls – in particular the role of temperature in driving changes in both $\delta^{18}O_P$ and $\delta^{18}O_{silica}$ can lead to difficulties in interpreting climate change from $\delta^{18}O_{silica}$ records. The holistic modelling approach taken here is proposed as a suitable means of addressing such complexities, enabling a more

detailed understanding of the limitations in the interpretation procedure and the use of sediment palaeoclimate records in a more rigorous, hypothesis testing format. However uncertainties concerning the controls over $\delta^{18}O_{silica}$ remain. In particular, the effect of temperature over the fractionation of oxygen isotopes between silica and water is still not fully quantified. In addition, factors such as the effects of diatom taxon, growth rate and chemical factors such as pH, salinity and nutrient limitation are yet to be addressed. Other important issues concern changes in the temporal pattern of seasonal diatom abundance, which can have large effects on predicted sediment $\delta^{18}O_{silica}$ values and the factors which control oxygen isotope ratios in precipitation – which remain only partially quantified. In both cases, adaptation of mechanistic models should lead to marked improvements in interpretative capabilities, however further data are required to aid their development. Although these issues hinder the rigorous interpretation of lake sediment $\delta^{18}O_{silica}$ to some extent, the primary limitation remains the ability to extract pure diatom silica from sediments in order to achieve reliable archives of past climate change.

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Appendix 1 Oxygen and hydrogen isotope composition of meteoric waters.sampled at Lochnagar between 1/12/1999 and 19/9/2005. Values expressed in per mille (‰) relative to V-SMOW.

Date	Days (post 1/1/2000)	INFLOW $\delta^{18}O$	INFLOW $\delta^{2}H$	OUTFLOW $\delta^{18}O$	OUTFLOW $\delta^{2}H$	PRECIPITATION $\delta^{18}O$	PRECIPITATION $\delta^{2}H$	SNOW $\delta^{18}O$	SNOW $\delta^{2}H$
01/12/1999	-30.0			-8.3	-55.0				
05/05/2000	126.0			-9.3	-61.7				
17/05/2000	138.0			-9.3	-61.4				
31/05/2000	152.0			-9.3	-62.0				
14/06/2000	166.0			-9.2	-60.9				
28/06/2000	180.0			-9.2	-60.4				
12/07/2000	194.0			-9.1	-60.4				
26/07/2000	208.0			-9.0	-61.0				
09/08/2000	222.0			-8.9	-58.9				
23/08/2000	236.0			-8.9	-59.8				
06/09/2000	250.0			-8.8	-57.9				
20/09/2000	264.0			-8.8	-58.7				
04/10/2000	278.0			-8.7	-59.6				
18/10/2000	292.0			-8.9	-60.2				
26/10/2000	300.0	-9.5	-63.4	-8.8	-60.2				
01/11/2000	306.0			-8.8	-59.3				
15/11/2000	320.0	-10.1	-69.1	-9.0	-61.3				
29/11/2000	334.0	-11.1	-75.1	-9.1	-61.9				
13/12/2000	348.0	-10.4	-71.6	-9.4	-62.9				
10/01/2001	376.0			-9.7	-65.0				
24/01/2001	390.0			-9.8	-65.5				
21/02/2001	418.0			-9.9	-65.1			-3.3	-6.7
20/03/2001	445.0			-10.1	-67.4			-9.5	-56.9
05/04/2001	461.0			-10.0	-65.7			-5.9	-28.3
20/04/2001	476.0			-10.0	-66.5			-4.9	-25.7
02/05/2001	488.0	-10.9	-72.0	-10.0	-66.4			-9.9	-61.5
16/05/2001	502.0	-10.4	-68.9	-9.7	-64.7				
30/05/2001	516.0	-10.4	-68.8	-9.7	-64.4				
13/06/2001	530.0	-10.3	-71.4	-9.7	-63.7				
27/06/2001	544.0	-9.7	-63.7	-9.6	-64.4				
11/07/2001	558.0	-9.8	-65.1	-9.6	-62.7				
25/07/2001	572.0	-9.4	-60.9	-9.5	-60.8				
08/08/2001	586.0	-9.3	-61.0	-9.4	-62.1				
22/08/2001	600.0	-8.9	-57.8	-9.2	-62.2	-8.1	-51.3		
05/09/2001	614.0	-8.9	-60.4	-9.2	-64.0	-9.4	-60.8		
19/09/2001	628.0	-8.9	-59.2	-9.1	-56.8	-8.5	-55.6		
03/10/2001	642.0	-8.5	-54.4	-9.0	-59.6	-7.4	-47.1		
17/10/2001	656.0	-8.3	-52.5	-8.9	-58.7	-8.2	-51.3		
01/11/2001	671.0	-8.2	-53.3	-8.8	-58.9	-7.6			
14/11/2001	684.0	-8.2	-53.1	-8.7	-57.4				
28/11/2001	698.0	-8.2	-53.3	-8.7	-57.5			-10.3	-61.2
12/12/2001	712.0	-8.9	-58.3	-8.7	-57.2	-9.5	-63.4		
08/01/2002	739.0	-9.2	-52.4	-8.7	-61.1	-9.4	-61.8		
23/01/2002	754.0	-9.1	-58.5	-8.7	-58.9	-8.1	-51.1	-18.4	-142.8
30/01/2002	761.0	-9.8	-64.7	-8.8	-58.1	-10.6	-70.7	-8.4	-56.2
13/02/2002	775.0	-10.0	-66.8	-9.0	-59.6	-10.6	-69.5	-6.4	-32.1
27/02/2002	789.0			-9.0	-60.9	-10.9	-76.4	-15.1	-106.8
13/03/2002	803.0			-9.4	-62.3			-8.4	-51.8
27/03/2002	817.0	-10.7	-71.8	-9.3	-61.5			-9.1	-63.4
10/04/2002	831.0	-10.5	-71.4	-9.2	-60.6				
24/04/2002	845.0	-10.0	-65.4	-9.2	-60.5				
08/05/2002	859.0	-10.2	-68.8	-9.2	-61.1				
22/05/2002	873.0	-9.3	-63.1	-9.2	-62.4	-8.3	-56.2		
05/06/2002	887.0	-9.3	-60.0	-9.1	-60.9	-9.3	-63.9		

Appendix 1 Oxygen and hydrogen isotope composition of meteoric waters.sampled at Lochnagar between 1/12/1999 and 19/9/2005. Values expressed in per mille (‰) relative to V-SMOW.

Date	Days (post 1/1/2000)	INFLOW $\delta^{18}O$	INFLOW $\delta^{2}H$	OUTFLOW $\delta^{18}O$	OUTFLOW $\delta^{2}H$	PRECIPITATION $\delta^{18}O$	PRECIPITATION $\delta^{2}H$	SNOW $\delta^{18}O$	SNOW $\delta^{2}H$
19/06/2002	901.0	-9.0	-60.8	-9.0	-62.7	-7.7	-52.4		
03/07/2002	915.0	-8.6	-60.6	-9.0	-61.4	-10.1	-72.3		
17/07/2002	929.0	-8.6	-57.7	-8.9	-59.5	-8.5	-58.2		
31/07/2002	943.0	-8.9	-60.3	-8.9	-61.8	-10.3	-71.1		
14/08/2002	957.0	-8.7	-59.5	-8.8	-58.7	-7.1	-45.8		
28/08/2002	971.0	-8.5	-56.9	-8.8	-59.5	-6.3	-38.8		
11/09/2002	985.0	-8.2	-53.1	-8.6	-57.7	-8.7	-60.5		
25/09/2002	999.0	-8.4	-56.6	-8.7	-57.7				
09/10/2002	1013.0	-7.8	-50.9	-8.5	-58.2	-6.0	-35.1		
24/10/2002	1028.0			-8.6	-57.9			-17.6	-129.8
06/11/2002	1041.0	-10.3	-67.5	-8.9	-60.9	-10.7	-70.7		
19/11/2002	1054.0	-9.6	-63.0	-9.1	-60.5	-11.3	-76.1		
04/12/2002	1069.0	-9.8	-62.9	-9.2	-59.0	-9.9	-64.4		
18/12/2002	1083.0			-9.2	-61.0			-7.6	-39.0
01/01/2003	1097.0	-9.6	-62.2	-9.3	-62.8	-16.8	-125.6	-16.7	
14/01/2003	1110.0	-9.3	-58.4	-9.3	-62.2	-9.2	-63.1		
12/02/2003	1139.0	-9.4	-60.5	-9.3	-61.6	-8.8	-60.6	-11.2	-79.2
26/02/2003	1153.0	-9.3	-59.3	-9.3	-60.5				
12/03/2003	1167.0	-9.1	-58.0	-9.2	-59.2	-8.4	-53.5	-7.0	-38.9
26/03/2003	1181.0	-9.1	-58.7	-9.2	-60.5	-7.6	-48.5		
09/04/2003	1195.0	-8.9	-57.5	-9.2	-59.3	-8.8	-63.6		
23/04/2003	1209.0	-8.9	-58.3	-9.2	-60.1	-9.5	-62.3		
07/05/2003	1223.0	-9.1	-62.2	-9.1	-61.4	-10.7	-76.1		
21/05/2003	1237.0	-8.9	-58.6	-9.1	-60.8	-8.4	-56.9		
04/06/2003	1251.0	-8.9	-59.5	-8.9	-61.3	-7.9	-56.3		
19/06/2003	1266.0	-8.7	-56.6	-8.9	-60.2	-6.6	-45.9		
02/07/2003	1279.0	-8.5	-55.3	-8.8	-57.9	-6.9	-44.7		
16/07/2003	1293.0	-8.7	-56.2	-8.7	-57.5	-5.6	-36.6		
30/07/2003	1307.0	-8.2	-55.3	-8.6	-59.6	-6.6	-43.4		
13/08/2003	1321.0	-8.3	-55.2	-8.4	-57.0	-5.3	-33.5		
27/08/2003	1335.0	-8.3	-56.0	-8.4	-57.6	-5.3	-31.7		
10/09/2003	1349.0	-8.1	-52.8	-8.4	-55.5	-7.4	-48.6		
24/09/2003	1363.0	-8.1	-49.4	-8.2	-57.2	-6.8	-43.8		
08/10/2003	1377.0	-7.7	-49.7	-8.1	-56.6	-8.7	-54.7		
23/10/2003	1392.0	-8.1	-53.1	-8.1	-56.8	-9.3	-56.0	-12.0	-73.7
05/11/2003	1405.0	-8.1	-51.6	-8.0	-55.8	-8.1	-48.5		
19/11/2003	1419.0	-8.4	-53.3	-8.9	-53.9	-10.5	-68.2		
03/12/2003	1433.0	-9.6	-62.1	-8.4	-55.4	-12.5	-89.3		
17/12/2003	1447.0	-9.2	-60.1	-8.2	-54.9	-11.4	-80.3		
03/01/2004	1464.0	-9.6	-64.1	-8.5	-57.7			-11.9	-85.7
13/01/2004	1474.0	-10.5	-70.6	-8.6	-58.5			-9.1	-56.6
12/02/2004	1504.0	-10.2	-66.7	-9.1	-59.7	-9.5	-65.1		
29/02/2004	1521.0			-9.0	-60.0			-5.8	-17.6
10/03/2004	1531.0			-9.1	-60.3			-5.4	-24.4
24/03/2004	1545.0			-8.9	-60.0			-6.0	-31.7
07/04/2004	1559.0	-9.2	-58.6	-9.0	-58.3	-8.6	-56.8	-9.1	-61.2
21/04/2004	1573.0	-9.3	-62.3	-9.0	-60.2	-11.0	-80.1		
05/05/2004	1587.0	-9.8	-67.5	-9.0	-60.3	-10.7	-74.6		
19/05/2004	1601.0	-9.4	-67.3	-9.0	-62.6	-9.2	-61.3		
02/06/2004	1615.0	-9.4	-62.2	-9.1	-59.1	-8.2	-52.3		
15/06/2004	1628.0	-9.3	-61.0	-8.9	-59.8	-7.3	-51.3		
30/06/2004	1643.0	-8.8	-59.1	-8.8	-59.1	-8.7	-59.0		
14/07/2004	1657.0	-9.0	-60.4	-8.7	-58.7	-8.1	-54.3		
28/07/2004	1671.0	-9.1	-60.7	-8.7	-59.4	-8.5	-58.5		

Appendix 1 Oxygen and hydrogen isotope composition of meteoric waters.sampled at Lochnagar between 1/12/1999 and 19/9/2005. Values expressed in per mille (‰) relative to V-SMOW.

Date	Days (post 1/1/2000)	INFLOW $\delta^{18}O$	INFLOW $\delta^{2}H$	OUTFLOW $\delta^{18}O$	OUTFLOW $\delta^{2}H$	PRECIPITATION $\delta^{18}O$	PRECIPITATION $\delta^{2}H$	SNOW $\delta^{18}O$	SNOW $\delta^{2}H$
11/08/2004	1685.0	-8.5	-57.3	-8.7	-59.0	-7.9	-53.4		
25/08/2004	1699.0	-8.5	-56.4	-8.6	-56.9	-9.1	-61.4		
08/09/2004	1713.0	-8.7	-57.7	-8.6	-57.0	-8.1	-52.8		
22/09/2004	1727.0	-8.4	-55.8	-8.5	-55.3	-7.8	-51.6		
06/10/2004	1741.0	-8.4	-55.3	-8.4	-56.4	-9.1	-60.8		
20/10/2004	1755.0	-8.8	-57.0	-8.4	-56.3	-9.8	-63.0	-16.0	-118.4
03/11/2004	1769.0	-9.3	-61.2	-8.6	-57.3	-11.2	-77.0		
17/11/2004	1783.0	-8.9	-58.5	-8.5	-57.3	-9.2	-63.1		
01/12/2004	1797.0	-9.2	-59.4	-8.5	-56.8	-10.4	-71.4		
15/12/2004	1811.0	-8.9	-58.1	-8.6	-56.5	-8.1	-57.5		
29/12/2004	1825.0	-9.1	-59.7	-8.5	-56.9			-11.0	-72.7
13/01/2005	1840.0	-9.4	-61.7	-8.7	-58.2			-6.2	-25.5
26/01/2005	1853.0	-9.0	-56.4	-8.7	-56.9			-9.1	-51.2
09/02/2005	1867.0	-8.5	-54.7	-8.6	-57.2				
09/03/2005	1895.0			-8.6	-57.4			-4.5	-24.1
23/03/2005	1909.0	-8.5	-54.6	-8.7	-56.5	-9.7	-65.7		
06/04/2005	1923.0	-8.6	-58.3	-8.8	-57.0	-9.7	-66.4		
15/04/2005	1932.0							-5.5	-29.4
20/04/2005	1937.0	-8.6	-56.3	-8.7	-56.9	-10.0	-68.6		
04/05/2005	1951.0	-8.6	-57.0	-8.6	-57.5	-9.8	-67.4		
18/05/2005	1965.0	-8.5	-56.3	-8.7	-57.6	-7.8	-50.6		
01/06/2005	1979.0	-8.9	-57.7	-8.6	-59.5	-9.4	-64.4		
15/06/2005	1993.0	-8.6	-59.8	-8.6	-59.1	-9.4	-67.2		
29/06/2005	2007.0	-8.5	-57.7	-8.5	-56.9	-5.0	-36.4		
13/07/2005	2021.0	-8.4	-57.0	-8.4	-56.9	-3.8	-27.2		
27/07/2005	2035.0	-8.5	-58.0	-8.3	-58.2	-6.9	-47.4		
10/08/2005	2049.0	-8.0	-53.5	-8.4	-56.0	-6.1	-38.3		
23/08/2005	2062.0	-8.2	-54.7	-8.2	-55.9	-8.1	-55.5		
07/09/2005	2077.0	-8.2	-54.2	-8.2	-54.0	-7.4	-48.7		
19/09/2005	2089.0	-8.0	-51.1	-8.0	-52.0	-6.4	-40.4		

Appendix 2 Diatom cell density and chlorophyll-a concentration for epilithon sampled at Lochnagar, 2004-2005.

Date	Sample	Site	Growth type	Diatoms with chloroplasts (cells/mm^2)						Diatoms without chloroplasts (cells/mm^2)						Chlorophyll-a (ng/mm^2)
				Achnanthes	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	*Achnanthes*	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	
05/05/2004	1	1	old	5.8	12.5	17.3	35.5	21.1	92.1	10.6	13.4	1.9	7.7	6.7	40.3	
05/05/2004	2	1	old	28.5	46.6	63.9	138.2	15.5	292.7	14.7	18.1	18.1	10.4	37.1	98.4	
02/06/2004	1	1	old	533.0	223.9	64.0	32.0	32.0	884.8	293.2	10.7	69.3	101.3	101.3	575.6	
15/06/2004	1	1	new	92.8	147.2	72.5	67.9	58.9	439.3	11.3	15.8	15.8	36.2	9.1	88.3	
15/06/2004	2	1	new	31.4	65.1	53.9	56.1	67.4	273.9	18.0	35.9	38.2	33.7	33.7	159.4	
15/06/2004	3	1	old	215.3	485.4	230.9	140.9	207.5	1280.0	90.0	86.1	317.1	172.2	78.3	743.7	
15/06/2004	4	1	old	97.4	591.6	180.4	187.6	165.9	1222.9	119.0	46.9	234.5	79.4	158.7	638.5	
30/06/2004	1	1	new	3.5	22.9	3.5	3.5	0.0	33.5	3.5	5.3	0.0	3.5	8.8	21.2	3.1
30/06/2004	2	1	new	3.5	30.0	17.7	14.1	22.9	88.3	1.8	3.5	1.8	0.0	3.5	10.6	15.7
30/06/2004	3	1	old	46.7	165.2	319.7	111.4	100.6	743.6	21.6	32.3	287.4	57.5	89.8	488.5	32.0
30/06/2004	4	1	old	105.1	79.7	271.7	47.1	126.8	630.4	58.0	68.8	268.1	72.5	90.6	557.9	87.2
28/07/2004	1	1	new	0.0	0.0	0.0	0.0	12.1	12.1	3.0	0.0	0.0	0.0	0.0	3.0	
28/07/2004	2	1	new	0.0	0.0	0.0	0.0	12.6	12.6	0.0	0.0	0.0	0.0	0.0	0.0	
28/07/2004	3	1	old	37.8	132.2	62.9	25.2	12.6	270.6	0.0	25.2	37.8	6.3	25.2	94.4	1.4
28/07/2004	4	1	old	67.5	94.6	81.1	13.5	13.5	270.2	33.8	67.5	33.8	20.3	27.0	182.4	2.1
25/08/2004	1	1	new	0.0	0.0	0.0	1036.7	0.0	1036.7	0.0	259.2	0.0	0.0	0.0	259.2	30.8
25/08/2004	2	1	old	116.1	132.6	0.0	16.6	24.9	290.1	107.8	82.9	33.2	0.0	91.2	315.0	78.0
25/08/2004	3	2	old	30.7	436.0	49.1	141.2	128.9	786.0	0.0	6.1	30.7	24.6	43.0	104.4	201.1
25/08/2004	4	3	old	36.8	12.3	61.4	1750.0	153.5	2014.0	0.0	6.1	12.3	202.6	12.3	233.3	100.5
22/09/2004	1	1	new	0.0	0.0	30.2	60.3	0.0	90.5	0.0	30.2	15.1	0.0	0.0	45.2	192.1
22/09/2004	2	1	new	15.5	0.0	31.0	93.0	0.0	139.5	0.0	62.0	15.5	0.0	62.0	139.5	172.7
22/09/2004	3	1	new	17.2	171.9	34.4	68.8	34.4	326.7	17.2	17.2	68.8	51.6	34.4	189.1	466.2
22/09/2004	4	1	old	0.0	66.3	33.2	596.8	0.0	696.3	66.3	0.0	99.5	215.5	82.9	464.2	334.8
22/09/2004	5	1	old	140.0	700.0	105.0	122.5	70.0	1137.5	52.5	70.0	70.0	52.5	35.0	280.0	345.5
22/09/2004	6	1	old	16.6	431.0	240.4	273.5	331.6	1293.1	16.6	66.3	24.9	58.0	41.4	207.2	504.0
22/09/2004	7	2	new	68.8	0.0	103.2	498.6	103.2	773.7	34.4	0.0	34.4	103.2	68.8	240.7	177.1
22/09/2004	8	2	new	185.7	33.8	135.1	624.8	101.3	1080.7	16.9	0.0	202.6	50.7	16.9	287.1	206.9
22/09/2004	9	2	new	58.9	147.4	147.4	324.2	736.8		0.0	73.7	58.9	88.4	147.4	368.4	
22/09/2004	10	2	old	132.6	132.6	294.7	309.5	383.2	1252.6	14.7	29.5	235.8	73.7	280.0	633.7	255.3
22/09/2004	11	2	old													91.5
22/09/2004	12	3	old													149.5
22/09/2004	13	3	new	54.6	409.9	0.0	232.3	54.6	751.4	13.7	27.3	0.0	0.0	0.0	41.0	28.1
22/09/2004	14	3	new	0.0	0.0	27.3	491.2	0.0	518.5	13.6	27.3	13.6	95.5	0.0	150.1	25.5
22/09/2004	15	3	new	24.6	257.9	24.6	1105.2	24.6	1436.8	0.0	49.1	36.8	110.5	12.3	208.8	

Appendix 2 Diatom cell density and chlorophyll-a concentration for epilithon sampled at Lochnagar, 2004-2005.

Date	Sample	Site	Growth type	Diatoms with chloroplasts (cells/mm^2)						Diatoms without chloroplasts (cells/mm^2)						Chlorophyll-a (ng/mm^2)
				Achnanthes	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	*Achnanthes*	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	
20/10/2004	1	1	new	61.7	41.1	41.1	205.7	473.1	822.8	0.0	10.3	0.0	20.6	0.0	30.9	153.2
20/10/2004	2	1	new	0.0	0.0	66.9	401.6	184.1	652.6	0.0	0.0	0.0	83.7	0.0	83.7	327.9
20/10/2004	3	1	new	48.4	0.0	64.5	854.3	0.0	967.1	16.1	16.1	16.1	32.2	64.5	145.1	359.2
20/10/2004	4	1	old	0.0	0.0	98.6	410.6	0.0	509.2	0.0	0.0	49.3	32.9	16.4	98.6	684.1
20/10/2004	5	1	old	35.3	247.1	105.9	617.9	0.0	1006.2	0.0	17.7	0.0	17.7	0.0	35.3	548.3
20/10/2004	6	1	old	56.5	254.2	28.2	1440.5	169.5	1948.9	14.1	56.5	14.1	268.3	14.1	367.2	677.5
20/10/2004	7	2	new	226.0	56.5	28.2	1482.9	141.2	1934.8	0.0	14.1	28.2	169.5	28.2	240.1	247.6
20/10/2004	8	2	new	16.4	0.0	32.9	1346.9	65.7	1461.8	0.0	0.0	32.9	82.1	0.0	115.0	204.2
20/10/2004	9	2	new	80.1	26.7	53.4	1028.3	80.1	1268.7	26.7	53.4	40.1	133.6	53.4	307.2	256.0
20/10/2004	10	2	old	210.6	0.0	240.7	2256.5	767.2	3475.1	15.0	30.1	105.3	315.9	240.7	707.0	558.4
20/10/2004	11	2	old													400.5
20/10/2004	12	2	old	350.0	36.8	755.2	3592.0	294.7	5028.9	147.4	55.3	147.4	128.9	128.9	607.9	390.3
20/10/2004	13	3	new	73.7	110.5	110.5	423.7	73.7	792.1	18.4	18.4	0.0	110.5	18.4	165.8	183.8
20/10/2004	14	3	new	110.5	221.0	36.8	1050.0	36.8	1455.2	18.4	0.0	18.4	36.8	18.4	92.1	141.2
20/10/2004	15	3	new	73.7	55.3	0.0	1215.8	810.5	2155.2	0.0	0.0	0.0	128.9	36.8	165.8	137.9
20/10/2004	16	3	old	0.0	0.0	147.4	2855.2	184.2	3186.8	0.0	18.4	110.5	184.2	36.8	350.0	279.0
20/10/2004	17	3	old	34.1	68.2	34.1	1073.5	136.3	1346.1	0.0	17.0	51.1	136.3	85.2	289.7	206.2
20/10/2004	18	3	old	101.3	287.1	135.1	3799.3	0.0	4322.7	0.0	33.8	16.9	287.1	135.1	472.8	120.4
17/11/2004	1	1	old													277.7
17/11/2004	2	1	old													315.9
17/11/2004	3	1	old													251.3
17/11/2004	4	1	new													68.9
17/11/2004	5	1	new													150.5
17/11/2004	6	1	new													200.6
17/11/2004	7	2	old													156.1
17/11/2004	8	2	old													707.1
17/11/2004	9	2	new													85.3
17/11/2004	10	2	new													216.7
17/11/2004	11	3	old													61.5
17/11/2004	12	3	new													132.5
23/03/2005	1	1	semi-new	133.9	117.1	334.6	669.3	301.2	1556.1	16.7	66.9	0.0	33.5	100.4	217.5	163.3
23/03/2005	2	1	semi-new	233.3	422.9	262.5	1181.2	87.5	2187.5	102.1	233.3	247.9	320.8	160.4	1064.6	210.5
23/03/2005	3	1	semi-new	0.0	1003.0	152.0	820.6	91.2	2066.8	30.4	106.4	136.8	136.8	182.4	592.7	205.7

Appendix 2 Diatom cell density and chlorophyll-a concentration for epilithon sampled at Lochnagar, 2004-2005.

Date	Sample	Site	Growth type	Diatoms with chloroplasts (cells/mm^2)						Diatoms without chloroplasts (cells/mm^2)						Chlorophyll-a (ng/mm^2)
				Achnanthes	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	*Achnanthes*	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	
23/03/2005	4	1	old	447.0	1468.7	1181.4	2394.7	223.5	5715.3	383.2	702.4	1101.6	686.5	622.6	3496.3	419.1
23/03/2005	5	1	old	52.2	6785.0	600.2	1043.8	247.9	8729.1	104.4	117.4	234.9	221.8	313.2	991.6	468.0
23/03/2005	6	1	old	291.7	3299.4	875.0	1895.8	364.6	6726.4	309.9	401.0	455.7	492.2	510.4	2169.2	556.9
20/04/2005	1	1	new	69.1	92.1	61.4	276.3	468.2	967.1	46.1	99.8	168.9	153.5	115.1	583.3	114.6
20/04/2005	2	1	new	62.0	155.0	62.0	31.0	31.0	341.1	62.0	0.0	31.0	46.5	0.0	139.5	96.2
20/04/2005	3	1	new	0.0	386.8	96.7	451.3	2627.3	3562.1	193.4	209.5	128.9	80.6	193.4	805.9	116.3
20/04/2005	4	1	old	246.4	887.0	772.0	1429.0	673.4	4007.7	197.1	230.0	443.5	739.1	344.9	1954.6	321.7
20/04/2005	5	1	old	295.7	1445.4	443.5	887.0	295.7	3367.2	312.1	689.9	574.9	492.8	985.5	3055.1	408.1
20/04/2005	6	1	old	497.4	2138.6	431.0	530.5	397.9	3995.5	464.2	646.6	580.3	480.8	630.0	2801.8	200.9
20/04/2005	7	2	old	488.1	2164.1	130.2	488.1	162.7	3433.3	260.3	244.1	406.8	537.0	520.7	1968.9	348.9
20/04/2005	8	2	old	423.7	141.2	317.8	1041.5	529.6	2453.8	582.6	494.3	459.0	494.3	300.1	2330.2	298.8
20/04/2005	9	2	old	488.1	650.9	390.5	943.8	244.1	2717.4	423.1	309.2	455.6	504.4	374.2	2066.5	373.0
20/04/2005	10	3	old	214.9	675.4	399.1	951.7	184.2	2425.4	629.4	368.4	644.7	414.5	399.1	2456.1	368.6
20/04/2004	11	3	old	876.8	2583.5	516.7	845.5	407.1	5229.6	532.4	344.5	642.0	767.2	1096.0	3382.0	288.6
20/04/2005	12	3	old	353.1	1384.0	480.2	734.4	113.0	3064.6	155.3	226.0	296.6	367.2	141.2	1186.3	358.2
22/05/2005	1	1	new	39.9	49.9	119.7	459.0	0.0	668.5	20.0	49.9	129.7	59.9	49.9	309.3	123.7
22/05/2005	2	1	new	141.2	264.8	70.6	423.7	70.6	970.9	53.0	105.9	105.9	53.0	53.0	370.7	87.4
22/05/2005	3	1	new	35.3	211.8	70.6	847.4	70.6	1235.7	88.3	0.0	88.3	88.3	194.2	459.0	94.4
22/05/2005	4	1	old	407.1	1816.3	814.2	1597.1	172.2	4806.9	563.7	250.5	673.3	1550.1	595.0	3632.6	502.2
22/05/2005	5	1	old	245.0	717.5	507.5	1120.0	105.0	2695.0	245.0	157.5	332.5	665.0	280.0	1680.0	287.6
22/05/2005	6	1	old	359.2	1097.6	359.2	1117.5	69.8	3003.3	169.6	89.8	439.0	568.7	179.6	1446.8	287.2
22/05/2005	7	2	new	77.4	128.9	154.7	257.9	90.3	709.2	141.8	38.7	219.2	257.9	77.4	735.0	55.4
22/05/2005	8	2	new	245.6	36.8	122.8	491.2	147.4	1043.8	147.4	24.6	343.9	196.5	245.6	957.9	37.6
22/05/2005	9	2	new	93.3	443.3	116.7	723.3	420.0	1796.6	35.0	81.7	233.3	46.7	116.7	513.3	59.1
22/05/2005	10	2	old	466.7	1954.1	583.3	1633.3	583.3	5220.7	437.5	87.5	875.0	875.0	700.0	2974.9	711.4
22/05/2005	11	2	old	158.4	1161.7	211.2	765.7	158.4	2455.5	237.6	158.4	528.1	580.9	237.6	1742.6	419.3
22/05/2005	12	2	old	184.2	368.4	890.3	1443.0	767.5	3653.4	184.2	491.2	828.9	982.4	644.7	3131.5	702.6
22/05/2005	13	3	old	863.3	840.6	408.9	2181.0	159.0	4452.9	249.9	227.2	1045.1	1113.2	227.2	2862.6	156.5
22/05/2005	14	3	old	618.9	438.4	257.9	1186.3	51.6	2553.1	180.5	103.2	309.5	567.4	335.3	1495.8	155.9
22/05/2005	15	3	old	353.1	0.0	635.5	1376.9	70.6	2436.1	282.5	282.5	847.4	670.8	35.3	2118.4	199.2
15/06/2005	1	1	new	101.9	0.0	0.0	101.9	0.0	203.9	0.0	0.0	203.9	203.9	0.0	407.7	34.9
15/06/2005	2	1	new	42.4	0.0	169.6	42.4	0.0	254.4	0.0	42.4	0.0	84.8	0.0	127.2	53.9
15/06/2005	3	1	new	35.6	0.0	106.8	89.0	0.0	231.5	0.0	0.0	71.2	71.2	17.8	160.3	22.2

Appendix 2 Diatom cell density and chlorophyll-a concentration for epilithon sampled at Lochnagar, 2004-2005.

Date	Sample	Site	Growth type	Diatoms with chloroplasts (cells/mm^2)						Diatoms without chloroplasts (cells/mm^2)						Chlorophyll-a (ng/mm^2)
				Achnanthes	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	*Achnanthes*	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	
15/06/2005	4	1	old	133.6	467.4	133.6	89.0	44.5	868.1	200.3	222.6	333.9	445.2	244.8	1446.8	117.4
15/06/2005	5	1	old	89.0	712.3	178.1	244.8	0.0	1224.2	111.3	66.8	289.4	44.5	111.3	623.2	120.6
15/06/2005	6	1	old	353.1	564.9	494.3	423.7	282.5	2118.4	423.7	317.8	317.8	741.4	459.0	2259.6	176.2
15/06/2005	7	2	new	70.3	210.9	70.3	46.9	70.3	468.6	82.0	0.0	35.1	128.9	82.0	328.0	
15/06/2005	8	2	new	50.4	0.0	75.7	126.1	25.2	277.4	50.4	25.2	88.3	50.4	50.4	264.8	34.6
15/06/2005	9	2	new	54.4	0.0	27.2	54.4	0.0	136.1	40.8	27.2	27.2	95.2	0.0	190.5	19.2
15/06/2005	10	2	old	71.8	1580.5	1005.8	1580.5	215.5	4454.1	323.3	287.4	718.4	1041.7	143.7	2514.4	217.6
15/06/2005	11	2	old	284.9	4344.8	854.7	2279.3	569.8	8333.5	356.1	356.1	463.0	997.2	463.0	2635.4	231.6
15/06/2005	12	2	old	245.0	2520.0	350.0	770.0	140.0	4024.9	210.0	140.0	280.0	735.0	280.0	1645.0	93.6
15/06/2005	13	3	new	6.4	12.7	38.2	127.2	12.7	197.1	6.4	0.0	31.8	63.6	57.2	159.0	
15/06/2005	14	3	new	25.9	155.3	12.9	64.7	0.0	258.8	0.0	6.5	19.4	6.5	0.0	32.3	
15/06/2005	15	3	new	0.0	0.0	0.0	76.3	0.0	76.3	6.4	6.4	38.2	19.1	0.0	70.0	3.2
15/06/2005	16	3	old	494.3	847.4	247.1	529.6	211.8	2330.2	706.1	229.5	494.3	335.4	176.5	1941.8	103.8
15/06/2005	17	3	old	794.4	158.9	141.2	35.3	229.5	1359.3	282.5	282.5	229.5	247.1	0.0	1041.5	61.3
15/06/2005	18	3	old	379.2	1137.5	145.8	495.8	758.3	2916.6	510.4	116.7	350.0	597.9	204.2	1779.1	113.7
13/07/2005	1	1	new	0.0	58.3	0.0	0.0	58.3	116.7	0.0	29.2	0.0	0.0	0.0	29.2	12.5
13/07/2005	2	1	new	0.0	0.0	29.7	0.0	0.0	29.7	44.5	14.8	89.0	0.0	0.0	148.4	22.2
13/07/2005	3	1	new	206.0	308.9	117.7	88.3	176.5	897.4	147.1	176.5	73.6	147.1	132.4	676.7	119.5
13/07/2005	4	1	old	105.9	1535.8	176.5	70.6	176.5	2065.4	317.8	141.2	105.9	158.9	317.8	1041.5	151.0
13/07/2005	5	1	old	88.3	476.6	141.2	194.2	670.8	1571.1	158.9	88.3	123.6	158.9	229.5	759.1	129.0
13/07/2005	6	1	old	212.8	2765.9	91.2	212.8	91.2	3373.8	121.6	152.0	288.7	364.7	197.6	1124.6	203.1
13/07/2005	7	2	new	35.3	0.0	0.0	53.0	35.3	123.6	17.7	0.0	53.0	70.6	70.6	211.8	514.3
13/07/2005	8	2	new	0.0	0.0	27.9	0.0	0.0	27.9	0.0	0.0	0.0	0.0	13.9	13.9	16.6
13/07/2005	9	2	new	26.4	52.8	0.0	0.0	0.0	79.2	26.4	0.0	66.0	66.0	26.4	184.7	13.4
13/07/2005	10	2	old	142.5	267.1	106.8	142.5	142.5	801.3	35.6	124.6	284.9	178.1	71.2	694.5	130.1
13/07/2005	11	2	old	142.5	320.5	178.1	178.1	142.5	961.6	71.2	71.2	338.3	284.9	124.6	890.3	218.9
13/07/2005	12	2	old	70.6	459.0	176.5	176.5	105.9	988.6	105.9	53.0	229.5	370.7	35.3	794.4	173.0
13/07/2005	13	3	new	0.0	153.1	21.9	0.0	0.0	175.0	10.9	10.9	21.9	10.9	10.9	65.6	15.6
13/07/2005	14	3	new	0.0	218.7	21.9	0.0	0.0	240.6	0.0	0.0	21.9	21.9	0.0	43.7	9.4
13/07/2005	15	3	new	80.6	172.7	23.0	0.0	0.0	276.3	92.1	46.1	138.2	80.6	23.0	379.9	14.1
13/07/2005	16	3	old	211.8	247.1	247.1	70.6	0.0	776.7	441.3	194.2	406.0	459.0	141.2	1641.7	119.5
13/07/2005	17	3	old	175.0	840.0	175.0	17.5	105.0	1312.5	280.0	70.0	210.0	402.5	52.5	1015.0	145.0
13/07/2005	18	3	old	388.4	105.9	0.0	35.3	0.0	529.6	211.8	35.3	35.3	105.9	35.3	423.7	89.7

Appendix 2 Diatom cell density and chlorophyll-a concentration for epilithon sampled at Lochnagar, 2004-2005.

Date	Sample	Site	Growth type	Diatoms with chloroplasts (cells/mm²)						Diatoms without chloroplasts (cells/mm²)						Chlorophyll-a (ng/mm²)
				Achnanthes	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	*Achnanthes*	*Aulacoseira*	*Eunotia*	*Tabellaria*	Other	TOTAL	
23/08/2005	1	1	new	79.6	29.9	0.0	0.0	19.9	129.4	0.0	0.0	0.0	10.0	19.9	29.9	56.8
23/08/2005	2	1	new	0.0	36.1	36.1	36.1	36.1	144.3	9.0	9.0	63.1	18.0	0.0	99.2	59.7
23/08/2005	3	1	new	17.8	35.7	0.0	0.0	0.0	53.5	44.6	17.8	26.8	0.0	35.7	124.9	80.6
23/08/2005	4	1	old	54.1	81.2	90.2	72.1	18.0	315.6	18.0	18.0	63.1	27.1	108.2	234.5	315.9
23/08/2005	5	1	old	112.8	48.4	177.3	16.1	16.1	370.7	16.1	32.2	88.6	80.6	24.2	241.8	436.6
23/08/2005	6	1	old	111.8	167.6	251.4	139.7	27.9	698.5	69.8	27.9	209.5	69.8	209.5	586.7	330.7
23/08/2005	7	2	new	12.5	0.0	0.0	0.0	0.0	12.5	0.0	0.0	37.6	0.0	0.0	37.6	93.8
23/08/2005	8	2	old	36.8	368.4	36.8	0.0	0.0	442.1	0.0	0.0	0.0	0.0	18.4	18.4	213.4
23/08/2005	9	3	new	62.0	0.0	124.0	124.0	155.0	465.1	108.5	62.0	93.0	77.5	248.1	589.2	
23/08/2005	10	3	old	164.7	1235.0	473.4	370.5	946.9	3190.5	185.3	185.3	720.4	267.6	432.3	1790.8	92.1
07/09/2005	1	1	new	17.7	0.0	0.0	17.7	17.7	53.0	35.3	8.8	8.8	8.8	17.7	79.4	25.2
07/09/2005	2	1	new	0.0	53.0	0.0	35.3	0.0	88.3	26.5	8.8	35.3	0.0	35.3	105.9	22.0
07/09/2005	3	1	new	22.1	110.3	66.2	22.1	22.1	242.7	33.1	44.1	22.1	0.0	22.1	121.4	44.0
07/09/2005	4	1	old	0.0	213.7	0.0	35.6	71.2	320.5	35.6	17.8	35.6	17.8	17.8	124.6	114.2
07/09/2005	5	1	old	401.9	365.3	146.1	0.0	73.1	986.4	91.3	127.9	91.3	146.1	146.1	602.8	110.7
07/09/2005	6	1	old	300.1	247.1	35.3	0.0	0.0	582.6	35.3	17.7	53.0	17.7	88.3	211.8	113.2
07/09/2005	7	2	new	0.0	0.0	0.0	47.9	0.0	47.9	8.0	16.0	0.0	8.0	0.0	31.9	52.2
07/09/2005	8	2	new	18.1	0.0	0.0	0.0	0.0	18.1	9.1	18.1	18.1	0.0	0.0	45.3	25.8
07/09/2005	9	2	new	0.0	0.0	17.0	25.6	0.0	42.6	25.6	25.6	34.1	8.5	0.0	93.7	10.1
07/09/2005	10	2	old	0.0	35.6	35.6	71.2	0.0	142.5	53.4	71.2	0.0	35.6	178.1	338.3	95.2
07/09/2005	11	2	old	135.1	878.1	270.2	315.2	180.1	1778.6	180.1	112.6	292.7	0.0	180.1	765.5	397.2
07/09/2005	12	2	old	0.0	423.1	65.1	130.2	195.3	813.6	32.5	65.1	97.6	48.8	81.4	325.4	180.4
07/09/2005	13	3	new	0.0	46.0	0.0	18.4	0.0	64.3	18.4	73.5	36.8	0.0	64.3	193.0	56.4
07/09/2005	14	3	new	22.1	187.6	22.1	0.0	44.1	275.8	0.0	44.1	11.0	0.0	11.0	66.2	44.0
07/09/2005	15	3	new	0.0	0.0	0.0	0.0	0.0	0.0	16.6	16.6	0.0	24.9	41.4	99.5	36.1
07/09/2005	16	3	old	144.9	0.0	36.2	0.0	36.2	217.4	108.7	90.6	108.7	72.5	217.4	597.8	135.6
07/09/2005	17	3	old	171.9	34.4	68.8	34.4	0.0	309.5	292.3	223.5	223.5	137.5	17.2	894.0	179.2
07/09/2005	18	3	old	407.7	420.5	0.0	51.0	191.1	1070.2	242.1	203.9	280.3	114.7	114.7	955.6	189.7

Appendix 3 Full diatom species list for taxa sampled in Lochnagar epilithon, 2004-2005. Codes apply to % relative abundance in Appendix 4.

Diatom taxon	Code	Diatom taxon	Code
Achnanthes aff. *amonea*	AC156A	*Achnanthes* aff. *amonea*	AC156A
Achnanthes altaica	AC046A	*Eunotia faba*	EU010A
Achnanthes altaica var .*minor*	AC046B	*Eunotia intermedia*	EU108A
Achnanthes detha	AC042A	*Eunotia major*	EU035A
Achnanthes grana	AC158A	*Eunotia minor*	EU110A
Achnanthes helvetica	AC134A	*Eunotia paludosa*	EU040A
Achnanthes helvetica var. *minor*	AC134C	*Eunotia pectinalis*	EU002A
Achnanthes helvetica var. *alpina*	AC134B	*Eunotia pectinalis* var. *undulata*	EU002D
Achnanthes lanceolata spp. *rostrata*	AC001B	*Eunotia pirla*	EU060A
Achnanthes marginulata	AC022A	*Eunotia praerupta*	EU003A
Achnanthes marginulata var. *major*	AC022C	*Eunotia praerupta* var. *bidens*	EU003B
Achnanthes minutissima	AC013A	*Eunotia praerupta* var. *bigibba*	EU003F
Achnanthes oblongella	AC143A	*Eunotia praerupta* var. *monodon*	EU003G
Achnanthes scotica	AC048A	*Eunotia perpusilla*	EU046C
Achnanthes linearis	AC002A	*Eunotia monodon* var. *bidens*	EU008D
Amphora aff. *ovalis*	AM001A	*Eunotia monodon* var. *monodon*	EU008A
Aulacosiera distans var. *nivalis*	AU005E	*Eunotia triodon*	EU039A
Aulacosiera distans var. *nivaloides*	AU005B	*Eunotia nygaardii*	EU998A
Aulacosiera lacustris	AU032A	*Eunotia nymannia*	EU045A
Aulacosiera distans var. *seppentrionalis*	AU9972	*Eunotia rhomboidea*	EU011A
Aulacosiera distans	AU005A	*Fragilaria brevistriata*	FR006A
Aulacosiera lirata	AU004A	*Fragilaria construens*	FR002A
Aulacosiera perglabra	AU010A	*Fragilaria construens* var. *binodis*	FR002B
Aulacosiera perglabra var. *florinae*	AU010B	*Fragilaria capucina*	FR009A
Aulacosiera tenella	AU028A	*Fragilaria exigua*	FR064Z
Brachysira brebessonii	BR006A	*Fragilaria parasitica*	FR045A
Brachysira vitrea	BR001A	*Fragilaria virescens*	FR005Z
Brachysira serians	BR003A	*Fragilaria voucheriae*	FR007A
Brachysira styriaca	BR004A	*Frustulia rhombiodes* var. *saxonica*	FU002B
Cocconeis placentula	CO001A	*Frustulia rhombiodes* var. *viridula*	FU002F
Cymbella hybrida var. *lanceolata*	CM008B	*Gomphonema accuminatum*	GO006A
Encyonopsis microcephala	ENC01A	*Gomphonema affine*	GO020A
Diatoma mesodon	DT021A	*Gomphonema angustatum*	GO003A
Diatoma tenius	DT004A	*Navicula angusta*	NA037A
Diploneis modica	DP067A	*Navicula bryophila*	NA045A
Encyonema borealis	CM046A	*Navicula capitata*	NA066A
Encyonema lunata	CM048A	*Navicula cryptotenella*	NA751A
Encyonema gracile	EY017A	*Navicula cryptocephala*	NA007A
Encyonema hebredica	EY003A	*Navicula contenta*	NA046A
Encyonema mesiana	EY010A	*Navicula krasskei*	NA044A
Encyonema minuta	EY011A	*Navicula radiosa*	NA003A
Encyonema schubartoides	EY999A	*Navicula shassmanii*	NA003B
Encyonema silesiaca	EY016A	*Navicula impexa*	NA068A
Encyonema perpusilla	EY014A	*Navicula indifferens*	NA016A
Eunotia incisa	EU047A	*Navicula mediocris*	NA006A
Eunotia subarcuatoides	EU105A	*Navicula pseudoscutiformis*	NA013A
Eunotia denticulata	EU015A	*Navicula rotunda*	NA090A
Eunotia curvata var. *subarcuata*	EU049B	*Navicula stroemii*	NA650A
Eunotia bilunaris	EU070A	*Navicula submeniscula*	NA134A
Eunotia diodon	EU016A	*Navicula subtilissima*	NA033A
Eunotia exigua	EU009A	*Navicula submolesta*	NA160A

Appendix 3 Full diatom species list for taxa sampled in Lochnagar epilithon, 2004-2005. Codes apply to % relative abundance in Appendix 4.

Diatom taxon	Code
Neidium alpinum	NE006A
Neidium affine	NE003A
Neidium affine var. *amphyrhyncus*	NE003C
Neidium affine var. *longiceps*	NE003B
Neidium ampliatum	NE036A
Neidium bisulcatum	NE004A
Neidium hernicynicum	NE020A
Nitzschia alpina	NI202A
Nitzschia microcephala	NI027A
Nitzschia palea	NI009A
Peronia fibula	PE002A
Pinnularia aboujensis	PI015A
Pinnularia aboujensis var. *lacustris*	PI015E
Pinnularia aboujensis var. *linearis*	PI015C
Pinnularia aboujensis var. *subundulata*	PI015D
Pinnularia biceps var. *pusilla*	PI018D
Pinnularia divergentissima	PI016A
Pinnularia divergens	PI008A
Pinnularia gibba	PI001A
Pinnularia major	PI005A
Pinnularia microstauron	PI011A
Pinnularia subcapitata	PI022A
Pinnularia aff. *terminata*	PI164A
Pinnularia turnerae	PI997
Pinnularia viridis	PI007A
Staurosira construens	SR001A
Staurosirella pinnata	SS002A
Stauroneis anceps	SA001A
Stauroneis kreigeri	SA012A
Stenopterobia delicatissima	SP005A
Stenopterobia curvula	SP006A
Suriella linearis (small)	SU005As
Suriella linearis (big)	SU005Ab
Suriella angustata	SU001A
Suriella constricta	SU030A
Tabellaria flocculosa	TA001Z
Tabellaria quadriseptata	TA004A
Tabellaria binalis	TA003A
Unknown	UNK
Chrysophyceae cysts	CC

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	Date	Sample	Growth	Site	AC156A	AC046A	AC046B	AC042A	AC158A	AC134A	AC134C
1	05/05/2004	1	old	1	0.47	0.93	0.00	0.00	0.00	4.21	3.27
2	05/05/2004	2	old	1	0.00	0.00	0.00	0.00	0.00	32.29	0.45
3	02/06/2004	1	old	1	0.00	0.00	0.44	0.00	0.00	9.73	3.54
4	15/06/2004	1	new	1	0.00	0.00	1.77	0.00	0.00	9.73	0.00
5	15/06/2004	2	new	1	0.00	0.00	0.00	0.00	0.00	14.00	2.80
6	15/06/2004	3	old	1	0.00	0.00	1.67	0.00	0.00	16.74	3.35
7	15/06/2004	4	old	1	0.00	0.00	0.00	0.00	0.00	12.80	14.22
8	30/06/2004	1	new	1	0.00	0.61	0.00	0.00	0.00	7.36	3.68
9	30/06/2004	2	new	1	0.00	0.00	0.00	0.00	0.00	8.02	6.75
10	30/06/2004	3	old	1	0.00	0.00	0.00	0.00	0.00	3.76	0.00
11	30/06/2004	4	old	1	0.00	0.00	0.47	0.00	0.00	4.25	6.60
12	28/07/2004	1	new	1	0.00	0.00	0.00	0.00	0.00	18.75	0.00
13	28/07/2004	2	new	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	28/07/2004	3	old	1	0.00	0.00	0.00	0.00	0.00	3.88	4.85
15	28/07/2004	4	old	1	0.00	0.00	0.50	0.00	0.00	8.42	1.49
16	25/08/2004	1	new	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	25/08/2004	2	old	1	0.00	0.00	0.00	0.00	0.00	5.62	0.80
18	25/08/2004	3	old	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	22/09/2004	1	new	1	0.00	0.00	0.39	0.00	0.00	2.72	1.95
20	22/09/2004	2	new	1	0.00	0.00	0.00	0.00	0.00	4.21	5.14
21	22/09/2004	3	new	1	0.00	0.00	0.00	0.00	0.00	2.35	2.82
22	22/09/2004	4	old	1	0.00	0.00	1.89	0.00	0.00	0.94	0.94
23	22/09/2004	5	old	1	0.00	0.00	1.35	0.00	0.00	4.95	3.15
24	22/09/2004	6	old	1	0.00	0.00	0.00	0.00	0.00	0.96	2.39
25	22/09/2004	7	new	2	0.00	0.00	0.00	0.00	0.00	1.95	0.00
26	22/09/2004	8	new	2	0.00	0.00	0.99	0.00	0.00	0.49	0.00
27	22/09/2004	9	old	2	0.00	0.00	0.00	0.00	0.00	1.95	0.00
28	22/09/2004	10	old	2	0.00	0.47	0.00	0.00	0.00	3.32	0.00
29	22/09/2004	13	new	3	0.00	0.00	0.49	0.49	0.00	0.49	0.49
30	22/09/2004	14	new	3	0.00	0.00	0.00	0.00	0.00	1.44	0.00
31	22/09/2004	15	old	3	0.00	0.00	0.00	0.00	0.00	0.00	0.95
32	20/10/2004	1	new	1	0.00	0.00	0.00	0.00	0.00	2.25	2.25
33	20/10/2004	2	new	1	0.00	0.00	0.00	0.47	0.00	0.95	0.00
34	20/10/2004	3	new	1	0.00	0.00	0.94	0.00	0.00	0.94	0.94
35	20/10/2004	4	old	1	0.00	0.00	0.00	0.00	0.00	0.00	0.48
36	20/10/2004	5	old	1	0.00	0.00	0.00	0.00	0.00	0.00	2.39
37	20/10/2004	6	old	1	0.00	0.00	0.00	0.00	0.00	0.00	0.95
38	20/10/2004	7	new	2	0.00	0.00	0.00	0.00	0.00	0.00	0.51
39	20/10/2004	8	new	2	0.00	0.00	0.47	0.00	0.47	0.00	0.95
40	20/10/2004	9	new	2	0.00	0.00	0.00	0.48	0.00	1.44	1.44
41	20/10/2004	10	old	2	0.00	0.00	0.00	0.00	0.00	0.00	0.48
42	20/10/2004	11	old	2	0.00	0.00	0.00	0.00	0.00	1.59	0.79
43	20/10/2004	12	old	2	0.00	0.00	0.47	0.00	0.00	0.93	0.00
44	20/10/2004	13	new	3	0.00	0.00	0.00	0.00	0.00	0.00	0.97
45	20/10/2004	14	new	3	0.00	0.00	0.00	0.00	0.00	0.00	0.99
46	20/10/2004	15	new	3	0.00	0.00	0.00	0.00	0.00	0.00	0.96
47	20/10/2004	16	old	3	0.00	0.00	0.00	0.00	0.00	0.00	0.95
48	20/10/2004	17	old	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	20/10/2004	18	old	3	0.00	0.00	0.00	0.00	0.00	0.47	0.00
50	23/03/2005	1	new	1	0.00	0.00	0.00	0.00	0.00	0.46	0.46

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	AC134B	AC001B	AC022A	AC022C	AC013A	AC143A	AC048A	AC002A	AM001A	AU005E	AU005B
1	0.00	0.00	19.63	2.80	0.47	0.00	0.00	0.00	0.00	20.09	0.00
2	0.00	0.00	13.45	0.45	0.00	0.00	0.00	0.00	0.00	8.97	0.00
3	0.00	0.00	21.68	0.44	0.00	0.00	0.00	0.00	0.00	8.41	0.00
4	0.00	0.00	16.37	0.00	0.44	0.00	0.00	0.00	0.00	12.83	0.00
5	0.00	0.00	15.60	2.00	0.00	0.00	0.00	0.00	0.00	7.20	6.40
6	0.00	0.00	22.59	0.84	0.00	0.00	0.00	0.00	0.00	6.28	0.00
7	0.95	0.00	12.32	3.32	0.00	0.00	0.00	0.00	0.00	9.95	0.95
8	1.23	0.00	21.47	0.61	0.00	1.84	0.00	0.00	0.00	9.82	7.36
9	0.00	0.00	18.14	1.27	0.00	0.00	0.00	0.00	0.00	23.21	2.95
10	0.00	0.00	11.29	0.00	0.00	0.00	0.00	0.00	0.00	16.13	0.00
11	3.77	0.00	16.98	0.47	0.00	0.00	0.00	0.00	0.00	9.91	0.94
12	0.00	0.00	25.00	0.00	6.25	0.00	0.00	0.00	0.00	6.25	0.00
13	2.22	0.00	13.33	0.00	0.00	0.00	0.00	0.00	0.00	4.44	0.00
14	0.00	0.00	23.30	0.97	0.00	0.00	0.00	0.00	0.00	17.96	3.40
15	2.48	0.00	25.25	0.50	0.00	0.00	0.00	0.00	0.99	17.82	0.00
16	0.00	0.00	11.54	0.00	3.85	0.00	0.00	0.00	0.00	34.62	0.00
17	0.40	0.00	11.65	0.00	0.00	0.00	0.00	0.00	0.00	31.73	14.06
18	0.00	0.00	1.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.39	0.00	26.07	0.39	0.00	0.00	0.00	0.00	0.00	24.12	3.11
20	1.87	0.00	23.83	0.93	0.00	0.00	0.00	0.00	0.00	16.82	2.80
21	0.00	0.00	22.07	1.88	0.47	0.00	0.00	0.00	0.00	28.64	0.00
22	1.89	0.00	12.26	2.36	0.00	0.00	0.00	0.00	0.00	22.17	4.25
23	0.00	0.00	16.67	1.35	0.00	0.00	0.45	0.00	0.00	16.67	3.15
24	2.39	0.00	13.88	0.48	0.00	0.00	0.00	0.00	0.00	21.05	0.00
25	0.49	0.00	8.29	0.49	0.00	0.00	0.00	0.00	0.00	11.71	0.00
26	0.49	0.00	3.94	0.00	0.00	0.00	0.00	0.00	0.00	3.45	0.00
27	0.00	0.00	5.37	0.00	0.00	0.00	0.00	0.00	0.00	1.95	0.00
28	0.00	0.00	8.06	0.00	0.00	0.00	0.00	0.00	0.00	6.64	0.00
29	0.00	0.00	6.86	0.49	0.00	0.00	0.00	0.00	0.00	3.92	1.96
30	0.00	0.00	1.92	0.00	0.00	0.00	0.00	0.00	0.00	0.96	0.00
31	0.48	0.00	0.95	0.00	0.00	0.00	0.00	0.00	0.00	1.90	0.00
32	0.00	0.00	1.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45
33	0.00	0.00	4.74	0.47	0.00	0.00	0.00	0.00	0.00	9.95	0.00
34	0.00	0.00	4.72	0.00	0.00	0.94	0.00	0.00	0.00	3.77	1.89
35	0.00	0.00	8.17	0.00	0.48	0.48	0.00	0.00	0.00	4.81	0.00
36	1.44	0.00	5.74	0.00	0.00	0.00	0.00	0.00	0.00	6.22	0.00
37	0.00	0.00	6.64	0.95	0.00	0.47	0.00	0.00	0.00	2.84	2.84
38	0.00	0.00	3.03	0.00	0.00	0.00	0.00	0.00	0.00	2.02	0.00
39	0.00	0.00	2.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.42
40	1.44	0.00	4.81	0.00	0.00	0.48	0.00	0.00	0.00	3.85	0.00
41	0.96	0.00	4.81	0.48	0.00	0.00	0.00	0.00	0.00	4.81	0.00
42	0.00	0.00	4.76	0.00	0.00	0.00	0.00	0.00	0.00	2.78	0.40
43	0.00	0.00	4.21	0.00	0.00	0.00	0.00	0.00	0.00	4.21	0.00
44	0.48	0.00	3.38	0.00	0.00	0.00	0.00	0.00	0.00	7.25	0.00
45	0.00	0.00	2.46	0.00	0.00	0.00	0.00	0.00	0.00	0.99	0.00
46	0.00	0.00	1.44	0.00	0.00	0.00	0.00	0.00	0.00	1.92	0.00
47	0.48	0.00	5.24	0.00	0.00	0.00	0.00	0.00	0.00	8.57	0.00
48	0.00	0.00	2.96	0.00	0.00	0.00	0.00	0.00	0.00	3.45	0.99
49	0.00	0.00	2.84	0.00	0.00	0.00	0.00	0.00	0.00	6.64	0.00
50	0.00	0.00	9.22	0.92	0.00	0.00	0.00	0.00	0.00	15.21	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	AU032A	AU9972	AU005A	AU004A	AU010A	AU010B	AU028A	BR006A	BR001A	BR003A	BR004A
1	0.00	0.93	1.40	0.00	0.00	0.00	0.00	1.40	0.00	0.00	0.00
2	1.35	0.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.44	0.88	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.00	0.00
4	0.00	1.33	0.00	0.00	0.00	0.00	1.33	1.33	0.00	0.00	0.00
5	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.80	0.00	0.00	0.00
6	0.00	1.26	0.00	0.00	0.00	0.00	4.18	1.26	0.00	0.00	0.00
7	0.00	3.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.61	1.23	0.00	0.00	0.00	0.00	0.61	0.61	0.00	0.00	0.00
9	0.84	2.11	0.00	0.00	0.00	0.00	1.69	0.84	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	1.89	0.00	0.00	0.00	0.00	0.00	2.83	0.47	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.25	0.00	0.00	0.00
13	2.22	2.22	0.00	0.00	0.00	0.00	0.00	2.22	0.00	0.00	0.00
14	0.49	0.00	0.00	0.00	0.00	0.00	0.00	1.94	0.00	0.00	0.00
15	0.50	1.49	0.00	0.00	0.00	0.00	3.47	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.85	0.00	0.00
17	0.40	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.48	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00
19	0.39	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	1.87	0.47	0.00	0.00	0.00	0.00	1.87	0.93	0.00	0.00	0.00
21	2.82	1.41	0.00	0.00	0.00	0.00	1.88	0.00	0.47	0.00	0.00
22	0.47	0.00	0.00	0.00	0.00	0.00	1.89	0.00	0.00	0.00	0.00
23	0.90	0.00	0.00	0.00	0.00	0.00	0.90	0.90	0.00	0.00	0.00
24	1.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.98	0.00	0.00
26	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.29	0.00	0.00	0.00
28	2.37	1.42	0.00	0.00	0.00	0.00	0.47	5.69	0.00	0.00	0.00
29	0.49	0.49	0.00	0.00	0.00	0.00	0.00	3.43	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00
34	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.48	0.48	0.00	0.00	0.00	0.00	0.96	0.96	0.00	0.00	0.00
36	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.51	2.02	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.48	0.00	0.00	0.00	0.00	0.00	0.00	2.40	0.00	0.00	0.00
41	0.00	0.48	0.00	0.00	0.00	0.00	0.00	3.37	0.48	0.00	0.48
42	0.00	0.40	0.00	0.00	0.00	0.00	0.00	5.16	0.00	0.00	0.00
43	0.93	0.00	0.00	0.00	0.00	0.00	0.00	5.14	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.00	0.48	3.86	0.00	0.00	0.00
45	0.49	0.49	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00
47	0.48	0.48	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.00
49	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	2.30	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	CO001A	CM008B	ENC01A	DT021A	DT004A	DP067A	CM046A	CM048A	EY017A	EY003A	EY010A
1	0.00	0.00	0.47	0.00	0.00	0.00	0.93	0.00	0.00	1.40	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.45	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.00	0.44	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.80	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.47	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.61	0.00	0.00	0.61	0.00
9	0.00	0.00	0.00	0.42	0.42	0.00	0.42	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.54	0.00	0.00	0.54	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	2.22	2.22	0.00	0.00	2.22	0.00	0.00	0.00	0.00
14	0.00	0.00	0.49	0.49	0.00	0.00	0.97	0.00	0.00	0.00	0.00
15	0.00	0.00	0.50	0.99	0.00	0.00	0.00	0.00	0.00	1.49	0.00
16	0.00	0.00	3.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.93	0.00	0.00	0.93	0.00
21	0.00	0.00	0.47	0.00	0.00	0.00	0.47	0.00	0.00	0.47	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	1.44	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.47	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.98	0.00	0.00	0.49	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00
32	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	1.01	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.96	0.00
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EY011A	EY999A	EY016A	EY014A	EU047A	EU105A	EU015A	EU049B	EU070A	EU016A	EU009A
1	0.00	0.00	0.00	0.00	6.07	1.87	0.47	0.00	0.00	0.00	0.47
2	0.00	0.00	0.00	0.45	3.59	1.79	0.00	0.90	0.00	0.00	0.00
3	0.00	0.00	0.00	0.44	0.88	13.72	0.00	0.00	0.00	0.00	0.44
4	0.00	0.00	0.00	0.00	4.42	10.62	0.88	0.44	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	6.40	10.00	0.40	0.80	0.00	0.00	0.40
6	0.00	0.00	0.00	0.00	1.26	11.30	0.00	0.00	0.00	0.00	0.84
7	0.00	0.00	0.00	0.00	1.90	15.17	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	3.68	7.36	0.61	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	3.38	5.49	0.42	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	2.15	38.17	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	2.83	31.60	0.94	0.00	0.00	0.00	0.47
12	0.00	0.00	0.00	0.00	6.25	6.25	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	4.44	11.11	13.33	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	4.85	6.80	3.40	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	6.93	7.92	0.00	0.99	0.00	0.00	0.50
16	0.00	0.00	0.00	0.00	0.00	19.23	23.08	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	4.82	6.83	2.01	0.00	0.00	0.00	0.40
18	0.00	0.00	0.00	0.00	1.43	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	1.95	1.95	0.39	0.39	0.00	0.00	0.39
20	0.00	0.00	0.00	0.00	6.07	1.87	1.87	0.00	0.00	0.00	0.93
21	0.00	0.00	0.00	0.00	4.69	3.76	0.94	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	2.36	0.00	0.94	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	4.50	2.25	0.00	0.00	0.00	0.00	1.35
24	0.00	0.00	0.00	0.00	5.26	2.87	1.44	0.48	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	7.80	0.49	0.49	1.46	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	14.29	0.99	5.42	0.99	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	10.24	1.46	2.93	1.95	0.00	0.00	0.49
28	0.00	0.00	0.00	0.47	10.90	3.32	5.21	2.84	0.00	0.00	4.27
29	0.00	0.00	0.00	0.00	7.35	0.00	2.94	0.00	0.00	0.00	0.98
30	0.00	0.00	0.00	0.00	2.40	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	3.81	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	1.80	1.35	0.90	0.00	0.00	0.00	0.90
33	0.00	0.00	0.00	0.00	1.42	1.42	0.47	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	1.89	0.94	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.48	2.88	4.33	1.92	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	1.91	14.35	0.48	0.00	0.00	0.00	1.91
37	0.00	0.00	0.00	0.00	1.90	4.74	0.95	0.00	0.00	0.00	1.42
38	0.00	0.00	0.00	0.00	4.04	3.54	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.47	0.47	0.95	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00	4.81	0.96	2.88	0.96	0.00	0.00	0.00
41	0.00	0.00	0.00	0.96	6.25	1.92	2.88	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.40	11.11	2.78	0.00	1.98	0.00	0.00	0.00
43	0.00	0.47	0.00	0.00	5.14	0.00	0.47	1.87	0.00	0.00	0.47
44	0.00	0.48	0.00	0.00	1.93	0.00	0.48	1.45	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.99	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	4.33	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	1.97	1.48	2.46	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	1.90	0.00	0.00	0.47	0.00	0.00	0.00
50	0.00	0.92	0.46	0.00	10.14	2.30	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EU010A	EU108A	EU035A	EU110A	EU040A	EU002A	EU002D	EU060A	EU003A	EU003B	EU003F
1	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.93	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
3	0.00	7.52	0.00	0.00	0.88	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.88	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	2.36	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.94	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.98	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EU003G	EU046C	EU008D	EU008A	EU039A	EU998A	EU045A	EU011A	FR006A	FR002A	FR002B
1	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
2	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00
6	0.00	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	0.00	12.62	0.00	0.00	0.00	0.00	0.00
15	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	FR009A	FR064Z	FR045A	FR005Z	FR007A	FU002B	FU002F	GO006A	GO020A	GO003A	NA037A
1	0.00	0.00	0.00	0.47	0.00	0.93	0.00	0.00	0.00	0.00	0.00
2	0.00	0.45	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00	0.00
3	0.00	1.33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.44	0.88	0.00	0.00	0.00	0.00
5	0.40	0.00	0.00	0.00	0.00	0.40	0.40	0.40	0.00	0.00	0.00
6	0.42	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	1.23	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	1.69	0.00	0.00	0.00	0.00	0.00
10	0.00	0.54	0.00	0.00	0.00	1.08	0.00	0.00	0.00	0.00	0.00
11	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	4.44	0.00	2.22	2.22	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	0.00	0.49	0.49	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	0.00	0.00	2.48	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.40	0.00	0.80	0.00	0.00	0.40	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	1.56	0.00	0.78	0.00	0.00	1.17	0.78	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.47	0.47	0.00	0.00	0.00	0.00
21	1.41	0.00	0.00	0.47	0.00	0.94	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
23	0.45	0.00	0.00	0.00	0.00	0.45	0.45	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.99	1.97	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	3.90	0.49	0.00	0.00	0.00	0.00
28	0.47	0.00	0.00	0.00	0.00	6.64	1.42	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.49	1.96	1.47	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00
31	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	3.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	1.90	0.00	0.47	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.48	0.00	0.48	0.48	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.48	0.48	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	1.90	0.00	0.00	0.47	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00	0.00	0.96	1.92	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.48	0.00	0.96	0.00	0.00	0.00	0.00	0.00
42	0.00	0.79	0.00	2.38	0.40	3.57	1.19	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	2.80	2.34	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.97	0.00	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00	0.00	0.99	0.99	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.96	0.48	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.48	0.00	0.95	0.48	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	2.30	0.00	0.00	0.46	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NA045A	NA066A	NA751A	NA007A	NA046A	NA044A	NA003A	NA003B	NA068A	NA016A	NA006A
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.90	0.00	0.45	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.88	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.88	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42	1.26	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.95	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	6.25	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00
15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.90
24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.94	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.93
45	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NA013A	NA090A	NA650A	NA134A	NA033A	NA160A	NE006A	NE003A	NE003C	NE003B	NE036A
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.61
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.00	0.54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	1.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
22	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.45	0.00	0.00	0.90	0.45	0.00	0.00	0.00	0.00	0.00
24	0.00	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
30	0.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.42
40	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.96
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NE004A	NE020A	NI202A	NI027A	NI009A	PE002A	PI015A	PI015E	PI015C	PI015D	PI018D
1	0.00	0.00	0.00	0.00	0.00	0.93	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	2.69	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	1.77	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.44	0.00	0.44	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	1.23	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.00	0.00	0.00	0.00	0.00	1.98	0.00	0.00	0.00	0.00	0.00
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	1.43	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	3.90	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.00	4.43	0.00	0.49	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	7.80	0.00	0.00	0.00	0.00	0.00
28	0.00	0.00	0.00	0.00	0.00	5.69	0.00	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00	1.47	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
33	0.00	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.00	0.00	0.00
34	0.00	0.00	0.00	0.00	0.00	0.00	0.94	0.00	0.00	0.00	0.00
35	0.00	0.00	0.00	0.00	0.00	0.96	0.48	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	2.02	0.00	0.00	0.00	0.00	0.00
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.00	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.00	0.00
41	0.00	0.00	0.00	0.00	0.00	2.88	0.00	0.00	0.00	0.00	0.00
42	0.00	0.00	0.00	0.00	0.00	3.57	0.00	0.00	0.00	0.00	0.00
43	0.00	0.00	0.00	0.00	0.00	5.14	0.00	0.00	0.00	0.00	0.00
44	0.00	0.00	0.00	0.00	0.00	0.48	0.48	0.00	0.00	0.00	0.00
45	0.00	0.00	0.49	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.00	0.00	0.00	0.00	2.38	0.00	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	1.48	0.00	0.49	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	2.37	0.00	0.00	0.00	0.47	0.00
50	0.00	0.00	0.46	0.00	0.00	0.46	0.00	0.92	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	PI016A	PI008A	PI001A	PI005A	PI011A	PI022A	PI164A	PI997	PI007A	SR001A	SS002A
1	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.00	0.00	0.00	2.65
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	1.20	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.00	0.84
7	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.95
8	0.00	0.00	0.00	0.00	0.00	0.61	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.94	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.22
14	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.97
15	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00	0.99
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19	0.00	0.00	0.00	0.00	0.39	0.00	0.00	0.00	0.00	0.00	0.00
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.34
21	0.47	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
22	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.45	0.00	0.00
24	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00
25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
26	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28	0.95	0.00	0.00	0.00	0.47	0.47	0.00	0.00	0.00	0.00	0.00
29	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.26
33	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.27
34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.42
35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.47	0.00	0.00
38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.05
39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.58
40	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	2.88
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.40
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.59
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.28
44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.43
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.96
47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	1.43
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.91
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	SA001A	SA012A	SP005A	SP006A	SU005As	SU005Ab	SU001A	SU030A	TA001Z	TA004A	TA003A	UNK	CC
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	19.16	0.00	0.00	4.21	3.27
2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.83	0.00	0.00	1.79	3.14
3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.27	0.00	0.00	4.87	2.65
4	0.00	0.00	0.00	0.00	1.33	0.00	0.00	0.00	21.24	0.00	0.00	11.06	24.34
5	0.00	0.00	0.00	0.00	0.40	0.40	0.00	0.00	17.20	0.00	0.00	10.40	28.80
6	0.00	0.00	0.00	0.00	2.09	0.00	0.00	0.00	10.88	0.00	0.00	8.79	12.97
7	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	12.32	0.00	0.00	5.21	15.64
8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.43	0.00	0.00	10.43	13.50
9	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	13.50	0.00	0.00	4.22	15.61
10	0.00	0.00	0.00	0.54	0.00	0.00	0.00	0.00	13.98	0.00	0.00	8.06	6.45
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.43	0.00	0.00	0.94	15.09
12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	18.75	0.00	0.00	0.00	25.00
13	0.00	0.00	0.00	0.00	4.44	0.00	0.00	0.00	8.89	0.00	0.00	0.00	15.56
14	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	6.31	0.00	0.97	0.97	10.19
15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.41	0.00	0.00	1.49	12.38
16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.85
17	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	10.04	0.00	0.00	5.62	18.07
18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	92.86	0.00	0.00	0.95	1.90
19	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.00	12.84	0.00	1.17	8.17	2.33
20	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	16.36	0.00	0.93	5.14	10.28
21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	13.15	0.00	0.00	3.76	18.31
22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	43.87	0.00	1.42	0.94	6.60
23	0.00	0.00	0.00	0.90	0.00	1.35	0.00	0.00	25.68	0.00	0.00	5.41	15.32
24	0.00	0.00	0.96	0.48	0.00	0.00	0.00	0.00	39.71	0.00	0.96	0.00	15.79
25	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	55.61	0.00	0.00	0.98	13.17
26	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.00	56.65	0.00	0.49	0.00	13.30
27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	52.20	0.00	0.00	0.49	6.83
28	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	23.22	0.00	0.00	2.84	18.96
29	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	59.80	0.00	0.00	0.49	5.88
30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	91.35	0.00	0.00	0.48	3.85
31	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	89.05	0.00	0.00	0.00	1.90
32	0.45	0.00	0.00	0.00	0.00	0.90	0.00	0.00	64.41	0.00	0.00	0.00	4.05
33	0.47	0.00	0.00	0.00	0.95	0.00	0.00	0.00	55.92	0.47	0.00	0.00	0.95
34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	76.89	0.00	0.00	0.00	1.89
35	2.88	0.00	50.96	0.00	11.54	0.48	0.00	0.00	0.00	0.00	0.00	1.92	3.85
36	0.00	0.00	0.00	0.00	0.00	0.48	0.48	0.00	59.81	0.00	0.00	2.39	3.35
37	0.00	0.00	0.00	0.00	0.00	0.95	0.00	0.00	72.51	0.47	0.00	0.00	2.84
38	0.00	0.00	0.00	0.00	0.00	0.00	0.51	0.00	75.25	0.51	0.00	0.00	1.52
39	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	74.41	0.95	0.00	0.95	0.00
40	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.00	62.50	0.00	0.00	0.48	4.81
41	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	59.13	1.44	0.00	0.48	4.81
42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	44.05	0.00	0.00	0.79	3.57
43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	51.87	0.00	0.00	1.87	4.21
44	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	71.98	0.00	0.00	0.97	7.73
45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	82.27	0.99	0.00	0.99	1.48
46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	87.02	0.48	0.00	0.96	1.44
47	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00	74.29	0.00	0.00	0.00	3.33
48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	71.92	0.49	0.00	0.99	2.96
49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	78.20	0.00	0.00	2.84	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	43.32	0.00	1.84	0.00	4.15

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	Date	Sample	Growth	Site	AC156A	AC046A	AC046B	AC042A	AC158A	AC134A	AC134C
51	23/03/2005	2	new	1	0.00	0.43	0.43	0.00	0.00	1.71	3.85
52	23/03/2005	3	new	1	0.00	0.00	0.00	0.00	0.00	2.88	1.65
53	23/03/2005	4	old	1	0.00	0.00	0.00	0.00	0.00	3.45	0.99
54	23/03/2005	5	old	1	0.00	0.00	0.00	0.00	0.00	1.69	0.85
55	23/03/2005	6	old	1	0.00	0.00	0.45	0.00	0.00	0.90	3.17
56	20/04/2005	1	new	1	0.00	0.41	0.41	0.00	0.00	1.24	2.07
57	20/04/2005	2	new	1	0.00	0.00	0.00	0.00	0.00	2.71	0.00
58	20/04/2005	3	new	1	0.00	0.00	0.00	0.00	0.00	4.09	0.91
59	20/04/2005	4	old	1	0.00	0.00	0.84	0.00	0.00	2.52	2.94
60	20/04/2005	5	old	1	0.00	0.00	0.45	0.00	0.00	4.04	4.93
61	20/04/2005	6	old	1	0.00	0.00	0.00	0.00	0.00	4.29	1.90
62	20/04/2005	12	old	2	0.00	0.00	0.82	0.00	0.00	8.64	4.53
63	22/05/2005	1	new	1	0.00	0.00	1.85	0.00	0.00	11.57	7.41
64	22/05/2005	2	new	1	0.00	0.45	0.91	0.00	0.00	9.09	5.91
65	22/05/2005	3	new	1	0.00	0.00	0.46	0.00	0.00	6.39	4.57
66	22/05/2005	4	old	1	0.00	0.00	1.95	0.00	0.00	2.72	5.84
67	22/05/2005	5	old	1	0.00	0.00	1.88	0.00	0.00	11.74	6.10
68	22/05/2005	6	old	1	0.00	0.00	1.42	0.00	0.00	5.21	6.16
69	22/05/2005	7	new	2	0.00	0.00	3.27	0.00	0.00	9.35	5.61
70	22/05/2005	8	new	2	0.00	0.00	0.88	0.00	0.00	7.46	3.07
71	22/05/2005	9	new	2	0.00	0.00	1.91	0.00	0.00	5.26	4.78
72	22/05/2005	10	old	2	0.00	0.00	0.84	0.00	0.00	2.51	2.93
73	22/05/2005	11	old	2	0.00	0.90	1.35	0.00	0.00	2.70	0.45
74	22/05/2005	12	old	2	0.00	2.38	0.00	0.00	0.00	4.76	5.24
75	22/05/2005	13	old	3	0.00	0.00	0.80	0.00	0.00	5.20	2.80
76	22/05/2005	14	old	3	0.00	0.00	0.91	0.00	0.00	3.65	4.11
77	22/05/2005	15	old	3	0.00	0.00	0.46	0.00	0.00	5.02	2.74
78	15/06/2005	1	new	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	15/06/2005	2	new	1	0.00	0.00	0.00	0.00	0.00	20.00	0.00
80	15/06/2005	3	new	1	0.00	0.00	0.00	0.00	0.00	4.26	0.00
81	15/06/2005	4	old	1	0.00	0.00	0.40	0.00	0.00	4.35	2.37
82	15/06/2005	5	old	1	0.00	0.00	0.00	0.00	0.00	5.38	2.69
83	15/06/2005	6	old	1	0.00	0.00	0.00	0.00	0.00	13.24	1.83
84	15/06/2005	7	new	2	0.00	0.00	0.88	0.00	0.00	5.26	0.88
85	15/06/2005	8	new	2	0.00	0.00	0.00	0.00	0.00	3.57	6.35
86	15/06/2005	9	new	2	0.00	0.00	0.99	0.00	0.00	4.46	0.99
87	15/06/2005	10	old	2	0.00	0.00	0.00	0.00	0.00	4.15	2.30
88	15/06/2005	11	old	2	0.00	0.00	1.43	0.00	0.00	1.43	5.24
89	15/06/2005	12	old	2	0.00	0.00	1.44	0.00	0.00	0.48	0.96
90	15/06/2005	13	new	3	0.00	0.00	0.00	0.00	0.00	0.00	2.33
91	15/06/2005	14	new	3	0.00	0.00	0.00	0.00	0.00	5.26	5.26
92	15/06/2005	15	new	3	0.00	0.00	0.00	0.00	0.00	0.40	2.83
93	15/06/2005	16	old	3	0.00	0.00	0.00	0.00	0.00	2.96	3.45
94	15/06/2005	17	old	3	0.00	0.00	5.06	0.00	0.00	2.53	5.49
95	15/06/2005	18	old	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	13/07/2005	1	new	1	0.00	0.00	0.00	0.00	0.00	1.49	1.49
97	13/07/2005	2	new	1	0.00	0.00	0.38	0.00	0.00	3.85	3.85
98	13/07/2005	3	new	1	0.00	0.00	1.85	0.00	0.00	6.02	6.48
99	13/07/2005	4	old	1	0.00	1.93	0.00	0.00	0.00	3.86	1.93
100	13/07/2005	5	old	1	0.00	0.00	0.78	0.00	0.00	5.45	4.67

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	AC134B	AC001B	AC022A	AC022C	AC013A	AC143A	AC048A	AC002A	AM001A	AU005E	AU005B
51	0.85	0.00	10.68	5.56	0.00	0.43	0.00	0.00	0.00	16.24	0.00
52	0.82	0.00	5.35	0.41	0.00	0.00	0.00	0.00	0.00	26.34	2.88
53	0.00	0.00	5.91	0.00	0.00	0.00	0.00	0.00	0.00	33.50	0.00
54	0.28	0.00	7.89	0.00	0.00	0.00	0.00	0.00	0.00	9.86	1.69
55	1.36	0.00	13.12	0.00	0.45	0.00	0.00	0.00	0.00	15.38	2.71
56	0.41	0.00	11.16	0.41	0.41	0.00	0.00	0.00	0.00	14.88	1.24
57	0.00	0.00	8.14	0.45	0.00	0.00	0.00	0.00	0.00	14.03	2.26
58	0.91	0.00	7.27	0.00	0.00	0.00	0.00	0.00	0.00	15.45	0.00
59	0.00	0.00	5.46	0.00	0.00	0.00	0.00	0.00	0.00	15.13	1.68
60	1.79	0.00	6.73	4.93	0.00	0.00	0.00	0.00	0.00	28.70	0.00
61	0.95	0.00	14.76	2.38	0.00	0.00	0.00	0.00	0.00	31.43	0.48
62	3.29	0.00	21.40	0.00	0.00	0.82	0.00	0.00	0.00	16.05	2.88
63	0.46	0.00	17.59	0.00	0.46	0.46	0.00	0.00	0.00	5.09	3.70
64	3.64	0.00	16.82	0.00	0.45	0.00	0.00	0.00	0.00	8.64	1.36
65	2.28	0.00	14.61	0.00	0.00	0.00	0.00	0.00	0.00	5.02	0.00
66	2.33	0.00	14.40	0.00	0.00	0.00	0.00	0.00	0.00	12.45	0.00
67	2.35	0.00	18.78	0.00	0.47	0.00	0.00	0.00	0.00	10.80	0.47
68	0.47	0.00	16.11	0.00	0.00	0.00	0.00	0.00	0.00	25.59	0.95
69	1.87	0.00	16.36	0.00	0.00	0.00	0.00	0.00	0.00	5.61	0.00
70	3.95	0.00	21.49	0.00	0.00	0.00	0.00	0.00	0.00	3.51	0.00
71	0.48	0.00	14.83	0.00	0.00	0.00	0.00	0.00	0.00	20.57	0.00
72	1.67	0.00	13.39	0.00	0.00	0.00	0.00	0.00	0.00	14.23	0.00
73	0.00	0.00	13.06	0.45	0.00	0.00	0.00	0.00	0.00	25.23	0.00
74	1.90	0.00	18.10	0.00	0.00	0.00	0.00	0.00	0.00	14.29	0.00
75	4.80	0.00	17.60	0.00	0.00	0.00	0.00	0.00	0.00	4.00	0.00
76	1.83	0.00	20.09	0.00	0.00	0.91	0.00	0.00	0.00	2.74	0.00
77	6.39	0.00	13.24	0.00	0.00	0.00	0.00	0.00	0.00	13.70	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	4.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	1.58	0.00	15.81	0.00	0.00	0.00	0.00	0.00	0.00	21.34	0.00
82	2.24	0.00	17.04	0.00	0.00	0.45	0.00	0.00	0.00	30.04	1.35
83	1.37	0.00	10.96	0.00	0.00	0.00	0.00	0.00	0.00	22.83	0.00
84	2.19	0.00	17.54	0.00	0.00	0.00	0.00	0.00	0.00	15.35	8.77
85	2.78	0.00	19.05	0.00	0.40	0.79	0.00	0.00	0.00	12.70	0.40
86	0.00	0.00	13.86	0.00	0.00	0.00	0.00	0.50	0.00	27.23	0.00
87	0.46	0.00	14.75	0.00	0.00	0.00	0.00	0.00	0.00	18.43	0.00
88	0.00	0.00	2.38	10.95	0.48	0.00	0.95	0.00	0.00	10.95	5.71
89	0.00	0.00	5.26	6.70	0.00	0.00	0.48	0.00	0.00	12.92	1.44
90	2.33	0.00	6.98	9.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	10.53	10.53	0.00	0.00	0.00	0.00	0.00	47.37	0.00
92	3.64	0.00	14.17	6.88	0.00	0.81	0.00	0.00	0.00	35.22	0.00
93	4.93	0.00	18.23	7.88	0.00	0.49	0.00	0.00	0.00	19.70	0.49
94	2.95	0.00	10.55	10.13	0.42	0.00	0.00	0.00	0.00	18.99	0.00
95	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	1.49	0.00	8.96	2.99	0.00	0.00	0.00	0.00	0.00	23.88	0.00
97	4.62	0.00	10.00	6.54	0.00	0.38	0.00	0.00	0.00	15.38	0.77
98	2.31	0.00	13.43	12.50	0.00	2.31	0.46	0.00	0.00	20.83	0.00
99	1.16	0.00	11.97	12.36	0.00	1.16	0.00	0.00	0.00	14.67	0.00
100	2.33	0.00	20.62	7.78	0.00	0.39	0.78	0.00	0.00	22.57	0.39

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	AU032A	AU9972	AU005A	AU004A	AU010A	AU010B	AU028A	BR006A	BR001A	BR003A	BR004A
51	0.85	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.43	0.00	0.00
52	0.82	0.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	1.48	0.49	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
54	0.28	3.10	0.00	0.00	0.00	0.00	2.54	0.28	0.28	0.00	0.00
55	0.45	4.07	0.00	0.00	0.00	0.00	0.45	0.45	0.00	0.00	0.00
56	3.31	0.41	0.00	0.00	0.00	0.00	0.00	0.83	0.00	0.00	0.00
57	0.45	1.36	0.00	0.00	0.00	0.00	0.00	1.36	0.00	0.00	0.00
58	0.45	0.45	0.00	0.00	0.00	0.00	4.09	0.91	0.00	0.00	0.00
59	1.68	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.45	1.79	0.00	0.00	0.00	0.00	3.59	0.90	0.00	0.00	0.00
61	0.48	3.81	0.00	0.00	0.00	0.00	1.90	1.43	0.48	0.00	0.00
62	0.82	0.82	0.00	0.00	0.00	0.00	1.65	0.41	0.00	0.00	0.00
63	1.39	2.31	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00
64	0.00	0.91	0.00	0.00	0.00	0.00	0.00	0.91	0.00	0.00	0.00
65	3.20	2.28	0.00	0.91	0.00	0.00	0.91	0.00	0.00	0.00	0.00
66	0.39	2.72	0.00	0.00	0.00	0.00	0.00	0.78	0.00	0.00	0.00
67	1.88	4.23	0.00	0.00	0.00	0.00	0.00	1.41	0.00	0.00	0.00
68	0.47	1.42	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.00	0.00
69	0.00	3.27	0.00	0.00	0.00	0.00	5.14	0.93	0.00	0.00	0.00
70	0.88	1.32	0.00	0.00	0.00	0.00	1.32	0.44	0.88	0.00	0.00
71	0.48	0.48	0.00	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00
72	0.00	0.42	0.00	0.00	0.00	0.00	0.00	0.84	0.42	0.00	0.00
73	5.41	0.00	0.00	0.00	0.00	0.00	0.00	0.90	0.45	0.00	0.00
74	0.00	1.90	0.48	0.00	0.48	0.00	0.00	0.48	0.00	0.00	0.00
75	0.40	0.40	0.00	0.00	0.80	0.00	0.00	0.80	0.00	0.00	0.00
76	0.91	0.91	0.00	0.00	0.00	1.83	0.00	0.00	0.46	0.00	0.00
77	0.00	0.91	0.00	0.00	0.91	0.00	1.83	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	25.53	0.00	0.00	0.00	0.00	0.00	0.00	4.26	0.00	0.00	0.00
81	0.00	3.16	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00
82	0.90	0.45	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00
83	0.46	3.65	0.00	0.00	1.37	0.00	1.37	0.91	0.00	0.00	0.00
84	0.44	0.00	0.00	0.00	0.00	3.51	0.00	0.88	0.00	0.00	0.00
85	0.00	0.79	0.00	0.00	0.00	0.00	0.00	1.98	0.40	0.00	0.00
86	0.50	2.48	0.00	0.00	0.00	0.00	0.00	2.48	0.00	0.00	0.00
87	0.00	8.29	0.00	0.00	0.00	0.00	0.00	2.76	0.00	0.00	0.00
88	1.90	0.48	0.00	0.00	0.00	0.48	0.95	1.90	0.00	0.00	0.00
89	0.00	2.39	0.00	0.00	0.00	1.44	0.00	0.96	0.00	0.00	0.00
90	2.33	0.00	0.00	0.00	0.00	0.00	0.00	2.33	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00
93	0.99	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.42	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	8.96	0.00	0.00	0.00	0.00	0.00	1.49	1.49	0.00	0.00
97	1.92	1.15	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	0.00
98	0.46	0.93	0.00	0.00	0.00	0.00	0.00	4.17	0.00	0.00	0.00
99	0.00	0.39	0.00	0.00	0.00	0.00	0.00	1.54	0.00	0.00	0.00
100	0.78	1.17	2.33	0.00	0.00	0.00	3.89	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	CO001A	CM008B	ENC01A	DT021A	DT004A	DP067A	CM046A	CM048A	EY017A	EY003A	EY010A
51	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.49	0.00	0.00	0.49	0.00	0.00	0.00	0.00
54	0.00	0.28	0.00	0.56	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	0.00	0.00	1.36	0.00	0.45	0.45	0.00
56	0.00	0.00	0.00	0.83	0.00	0.00	0.41	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.45	0.00
59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.00
60	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.45	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
62	0.00	0.00	0.00	0.41	0.00	0.00	1.23	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.93	0.00	0.00	0.46	0.00	0.00	0.00	0.00
64	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.78	0.00	0.00	0.00	0.00	0.00	0.00	0.00
67	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.47	0.00	0.00	0.95	0.00	0.00	0.00	0.00
69	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.42	0.84	0.00
73	0.00	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00
75	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00
82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.44	0.00	0.00
85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
86	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.50	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.78	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EY011A	EY999A	EY016A	EY014A	EU047A	EU105A	EU015A	EU049B	EU070A	EU016A	EU009A
51	0.00	0.00	0.00	1.28	8.97	0.85	0.00	0.43	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	6.17	2.06	0.00	0.41	0.00	0.00	0.00
53	0.00	0.00	0.49	0.00	5.91	5.42	0.00	0.49	0.00	0.00	0.00
54	0.00	0.00	0.28	0.28	3.94	1.97	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	2.71	9.05	0.00	0.90	0.00	0.00	0.00
56	0.00	0.00	0.00	0.00	7.85	0.41	0.00	0.41	0.00	0.00	0.00
57	0.00	0.00	0.00	0.45	8.14	4.98	0.45	0.90	0.00	0.00	0.45
58	0.00	0.45	0.00	0.00	9.55	2.27	0.91	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.42	3.78	13.45	0.00	0.00	0.00	0.00	0.00
60	0.00	0.00	0.45	0.00	8.07	1.35	1.35	0.00	0.00	0.00	0.45
61	0.00	0.00	0.00	0.00	4.76	3.81	0.00	0.48	0.00	0.00	0.00
62	0.00	0.00	0.41	1.23	5.35	2.88	0.41	0.00	0.00	0.00	0.41
63	0.00	0.00	0.93	0.46	1.39	7.87	0.46	2.78	0.00	0.00	0.00
64	0.00	0.00	0.45	1.36	5.45	4.09	0.45	1.36	0.00	0.00	0.45
65	0.00	0.00	1.37	0.00	5.02	3.20	0.00	0.00	0.00	0.00	1.83
66	0.00	0.00	0.78	0.39	1.17	5.06	0.39	0.00	0.00	0.00	0.39
67	0.00	0.00	0.47	0.47	5.16	6.10	0.00	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.95	4.74	5.21	0.00	0.00	0.00	0.00	0.00
69	0.00	0.00	0.47	0.00	8.88	6.07	0.93	0.00	0.00	0.00	0.00
70	0.00	0.00	1.32	0.00	8.33	2.63	1.75	0.00	0.00	0.00	0.44
71	0.00	0.00	0.00	0.00	3.83	4.78	0.48	1.44	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	5.86	2.51	0.42	0.84	0.00	0.00	0.00
73	0.00	0.00	1.35	0.45	7.66	1.35	1.35	0.90	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	6.19	2.38	3.33	0.48	0.00	0.00	0.48
75	0.00	0.00	2.00	0.00	0.80	8.00	0.00	0.40	0.00	0.00	0.40
76	0.00	0.00	0.00	0.00	4.57	2.28	0.00	0.46	0.00	0.00	0.00
77	0.00	0.00	0.00	0.00	4.11	3.20	0.91	1.83	0.00	0.00	0.46
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	4.26	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	4.74	6.32	0.00	0.00	0.00	0.00	0.00
82	0.00	0.00	0.90	0.00	2.69	4.48	0.00	0.00	0.00	0.00	0.00
83	0.00	0.46	0.00	0.00	3.20	4.57	0.91	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00	3.07	2.63	1.32	0.00	0.00	0.00	0.44
85	0.00	0.00	0.00	0.79	3.17	4.37	0.00	0.79	0.00	0.00	0.40
86	0.00	0.00	0.00	0.00	4.46	0.00	0.99	5.94	0.00	0.00	0.00
87	0.00	0.00	0.00	0.46	6.91	0.46	0.92	1.84	0.00	0.00	0.00
88	0.00	0.00	0.48	0.00	10.95	1.43	2.38	0.00	0.00	0.00	0.95
89	0.00	0.00	0.48	0.00	8.13	0.96	0.48	1.44	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	18.60	4.65	4.65	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	5.26	10.53	5.26	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	3.64	3.24	0.81	0.00	0.00	0.00	1.62
93	0.00	0.00	0.00	0.49	5.91	2.96	0.00	0.00	0.00	0.00	0.49
94	0.00	0.00	0.84	0.00	0.84	4.22	0.42	0.00	0.00	0.00	0.84
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	14.93	8.96	2.99	0.00	0.00	0.00	0.00
97	0.00	0.00	1.15	0.00	1.92	6.15	0.00	0.38	0.00	0.00	0.00
98	0.00	0.00	0.00	0.93	7.41	2.78	0.93	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.77	4.25	5.79	0.39	0.00	0.00	0.00	0.39
100	0.00	0.00	0.39	0.78	1.95	2.72	0.00	0.39	0.00	0.00	0.78

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EU010A	EU108A	EU035A	EU110A	EU040A	EU002A	EU002D	EU060A	EU003A	EU003B	EU003F
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	0.00	0.00	0.56	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
57	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.48	0.48	0.00	0.00	0.00	0.00	0.00
62	0.00	0.00	0.41	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00
63	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.00
67	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00
68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00
69	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45
74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.91	0.00
77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00	0.91	0.46	0.00	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
86	0.00	2.48	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
88	0.00	0.00	0.48	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
93	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EU003G	EU046C	EU008D	EU008A	EU039A	EU998A	EU045A	EU011A	FR006A	FR002A	FR002B
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56	0.00	0.00	0.00	0.00	0.00	0.00	0.83	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.42	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
69	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00
70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00
85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.49	0.00	0.00	1.49
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	FR009A	FR064Z	FR045A	FR005Z	FR007A	FU002B	FU002F	GO006A	GO020A	GO003A	NA037A
51	0.00	0.43	0.00	0.85	0.00	0.43	2.14	0.43	0.00	0.00	0.00
52	0.00	0.00	0.00	4.53	0.00	1.23	0.41	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	14.08	0.00	0.56	1.41	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	2.26	0.00	0.90	0.00	0.45	0.00	0.00	0.00
56	0.00	0.83	0.00	2.48	0.00	0.41	1.24	0.83	0.00	0.00	0.00
57	0.00	0.00	0.00	1.81	0.45	0.45	0.90	0.45	0.00	0.00	0.00
58	0.00	0.00	0.00	1.82	4.09	0.45	1.36	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	3.36	0.00	0.42	0.42	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.45	0.00	0.45	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.48	0.00	0.48	0.48	0.00	0.00	0.00	0.00
62	0.41	0.00	0.00	0.41	0.00	0.82	0.41	0.00	0.00	0.00	0.00
63	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	1.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.46	0.00	0.00	1.37	0.00	0.46	0.46	0.46	0.00	0.00	0.00
66	0.00	0.00	0.00	3.89	0.00	0.39	0.00	0.39	0.00	0.00	0.00
67	0.00	0.00	0.00	1.41	0.00	0.00	0.47	0.00	0.00	0.00	0.00
68	0.47	0.00	0.00	0.47	0.00	0.95	1.90	0.00	0.00	0.00	0.00
69	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70	0.44	0.00	0.00	4.39	0.00	2.19	1.75	0.44	0.00	0.00	0.44
71	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	3.35	0.00	0.42	0.42	0.00	0.00	0.00	0.00
73	0.45	0.00	0.00	2.25	0.00	0.45	1.35	0.00	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00	0.00
75	0.00	0.00	0.00	8.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00
76	0.91	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0.00	0.00	0.00	2.74	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	14.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	3.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82	0.00	0.45	0.00	2.24	0.00	0.00	0.45	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	2.74	0.00	0.00	0.46	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	1.75	0.00	0.44	0.00	0.00	0.00	0.00	0.00
85	0.00	0.00	0.00	6.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00
86	0.00	0.00	0.00	0.00	0.00	0.50	0.99	0.00	0.00	0.00	0.00
87	0.46	0.00	0.00	0.00	0.00	1.84	0.46	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.48	0.00	0.95	0.48	0.00	0.00	0.00	0.00
89	0.00	0.00	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	3.24	0.00	0.00	0.40	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.00	0.00	0.00
94	0.00	3.80	0.00	0.00	0.00	0.42	0.42	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	7.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.46	0.00	0.46	0.93	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	9.27	0.00	0.00	0.77	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	2.33	0.00	0.00	1.17	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NA045A	NA066A	NA751A	NA007A	NA046A	NA044A	NA003A	NA003B	NA068A	NA016A	NA006A
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	0.00	0.00	0.28	0.00	0.00	0.00	0.00	0.00
55	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45
56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
57	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42
60	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00
62	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00	0.00	0.00
63	0.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	0.45	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.45
65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39
67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
69	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.47	0.00
70	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	0.00	1.43	0.48	0.00	0.00	0.00	0.00
75	0.00	0.00	0.00	0.00	0.00	1.60	0.00	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	0.00	1.19	0.00	0.00	0.00	0.00	0.00
82	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.40
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.84	0.00	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	1.49	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.00	0.00	0.00	0.39
100	0.00	0.00	0.00	0.00	0.00	0.39	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NA013A	NA090A	NA650A	NA134A	NA033A	NA160A	NE006A	NE003A	NE003C	NE003B	NE036A
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
56	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.00	0.00
57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	0.00
63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.00	0.00	0.00	0.00
71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00
76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00	0.00	0.44	0.00	0.00	0.00	0.00	0.00
85	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NE004A	NE020A	NI202A	NI027A	NI009A	PE002A	PI015A	PI015E	PI015C	PI015D	PI018D
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49
54	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	0.45	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
56	0.00	0.00	0.00	0.00	0.00	0.83	0.00	0.00	1.24	0.00	0.41
57	0.00	0.00	0.00	0.00	0.00	1.36	0.00	0.00	0.45	0.00	0.45
58	0.00	0.00	0.00	0.00	0.00	1.36	0.00	0.00	0.45	0.00	0.00
59	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.00	0.00
60	0.45	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.90
61	0.48	0.00	0.00	0.00	0.00	1.43	0.00	0.00	0.00	0.00	0.00
62	0.00	0.00	0.00	0.00	0.00	1.23	0.00	0.00	0.00	0.00	0.41
63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.93
64	0.00	0.00	0.45	0.00	0.00	1.36	0.00	0.00	0.00	0.00	0.00
65	0.91	0.00	0.00	0.00	0.00	1.83	0.00	0.00	0.00	0.00	0.00
66	0.00	0.00	0.00	0.00	0.00	1.95	0.00	0.00	0.00	0.00	0.00
67	0.00	0.00	0.00	0.00	0.00	1.41	0.00	0.00	0.00	0.00	0.94
68	0.00	0.00	0.00	0.00	0.00	0.95	0.00	0.00	0.00	0.00	0.95
69	0.00	0.00	0.00	0.00	0.00	1.40	0.00	0.00	0.00	0.00	0.47
70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
71	0.48	0.00	0.00	0.00	0.00	0.96	0.00	0.00	0.00	0.48	0.00
72	0.42	0.00	0.00	0.00	0.00	1.26	1.26	0.00	0.00	0.00	0.00
73	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00
74	0.48	0.00	0.00	0.00	0.00	0.48	0.00	0.48	0.00	0.00	0.95
75	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.00	0.00	1.37	0.00	0.00	0.00	0.00	0.00
77	0.00	0.00	0.00	0.00	0.00	0.91	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.40	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.40
82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45
83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.91
84	0.88	0.00	0.00	0.00	0.00	0.44	0.44	0.00	0.00	0.00	0.00
85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.40
86	0.00	0.00	0.00	0.00	0.00	1.49	0.00	0.00	0.00	0.00	0.00
87	0.46	0.00	0.00	0.00	0.00	2.76	0.00	0.00	0.00	0.00	0.00
88	0.00	0.00	0.00	0.00	0.00	1.43	0.00	0.00	0.00	0.00	0.48
89	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	1.44	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	4.65	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.81
93	0.99	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.00	0.84
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.49	0.00	2.99
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38
98	0.00	0.00	0.00	0.00	0.00	1.85	0.00	0.00	0.00	0.00	0.46
99	0.00	0.00	0.00	0.00	0.00	0.77	0.00	0.00	0.00	0.00	0.00
100	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	PI016A	PI008A	PI001A	PI005A	PI011A	PI022A	PI164A	PI997	PI007A	SR001A	SS002A
51	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
54	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.56
55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.62
56	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.00	3.72
57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00
61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
62	0.00	0.00	0.00	0.00	0.00	0.00	0.82	0.00	0.00	0.00	3.70
63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	0.00	0.00	0.00	0.00	0.00	0.00	0.91	0.00	0.00	0.00	0.00
65	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46
66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
67	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	2.80
70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.75
71	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	2.87
72	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.28
73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
74	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	12.86
75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
76	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.90
83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.44
85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.98	13.10
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.38
88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48
89	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38
98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.33

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	SA001A	SA012A	SP005A	SP006A	SU005As	SU005Ab	SU001A	SU030A	TA001Z	TA004A	TA003A	UNK	CC
51	0.43	0.00	0.00	0.43	0.00	0.00	0.43	0.00	32.91	0.85	0.00	2.56	2.56
52	0.00	0.41	0.41	0.00	0.00	0.00	0.00	0.00	28.81	0.00	0.00	0.00	5.35
53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	38.42	0.00	0.00	0.00	2.46
54	0.28	0.00	0.28	0.00	0.00	0.00	0.00	0.00	17.46	0.00	0.00	0.00	0.85
55	0.00	0.00	0.00	0.00	1.36	0.45	0.45	0.00	23.53	0.00	0.00	0.90	7.24
56	0.41	0.00	0.83	0.41	0.00	0.41	0.00	0.00	27.69	0.00	0.00	0.00	1.65
57	0.00	0.00	0.90	0.00	0.45	0.00	0.00	0.00	36.20	0.00	0.00	3.62	6.33
58	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	30.45	0.45	0.00	0.45	6.36
59	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00	32.35	0.42	0.00	4.62	3.78
60	0.00	0.00	0.00	0.00	0.90	0.45	0.00	0.00	18.83	0.00	0.00	3.59	4.93
61	0.48	0.00	0.00	0.00	0.00	0.48	0.00	0.00	18.10	0.00	0.48	0.00	8.57
62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.40	0.00	0.00	0.00	10.70
63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	28.24	0.00	0.00	0.00	39.81
64	0.00	0.00	0.91	0.00	0.91	0.45	0.00	0.00	24.09	0.91	0.00	1.82	16.82
65	0.00	0.00	0.00	0.00	2.28	0.46	0.00	0.00	32.88	0.00	0.00	2.28	21.92
66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.29	0.00	0.00	3.89	11.67
67	0.00	0.00	0.00	0.94	0.00	0.00	0.00	0.00	16.43	0.00	0.00	1.88	8.92
68	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	17.06	0.95	0.00	2.37	8.06
69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	23.36	0.00	0.00	0.00	27.10
70	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	17.98	0.00	0.00	0.88	10.09
71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	31.58	0.00	0.00	0.96	13.40
72	0.00	0.00	0.42	0.00	0.42	0.00	0.42	0.00	25.94	0.00	0.00	2.09	11.30
73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	23.42	0.00	0.00	0.00	8.11
74	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	14.76	0.00	0.00	2.86	13.33
75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.80	0.00	0.00	0.80	13.20
76	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	46.12	0.00	0.00	1.83	14.16
77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	31.96	0.00	0.00	1.83	9.13
78	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	80.00	0.00	0.00	0.00	0.00
80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.51	0.00	0.00	4.26	10.64
81	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	10.67	0.00	0.00	0.79	9.49
82	0.00	0.00	0.00	0.00	1.35	0.45	0.00	0.00	17.49	0.00	0.00	0.00	6.73
83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.55	0.00	0.00	0.91	3.65
84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	26.32	0.00	0.00	0.00	10.09
85	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	4.37	0.00	0.00	0.00	5.56
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	27.72	0.00	0.00	0.00	4.95
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	27.65	0.00	0.00	0.00	6.91
88	0.00	0.00	0.00	0.00	0.95	0.48	0.00	0.00	29.05	0.00	0.00	0.00	8.10
89	0.00	0.00	0.00	0.00	1.91	0.00	0.00	0.00	45.93	0.00	0.00	0.96	6.70
90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	41.86	0.00	0.00	0.00	2.33
91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	12.15	0.00	0.00	0.40	4.86
93	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.12	0.00	0.00	0.99	4.93
94	0.00	0.00	0.00	0.42	0.84	0.00	0.00	0.00	12.66	0.00	0.00	1.69	5.91
95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.49	8.96	0.00	0.00	0.00	11.94
97	0.00	0.00	0.00	0.00	0.38	0.38	0.00	0.77	12.69	0.00	0.00	2.31	5.77
98	0.00	0.00	0.46	0.00	0.93	0.00	0.00	0.00	7.87	0.00	0.00	0.00	6.94
99	0.77	0.00	0.00	0.00	0.00	0.39	0.00	0.00	5.79	0.00	0.00	0.00	4.63
100	0.00	0.00	0.00	0.00	1.17	0.39	0.00	0.00	3.50	0.00	0.00	1.56	2.33

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	Date	Sample	Growth	Site	AC156A	AC046A	AC046B	AC042A	AC158A	AC134A	AC134C
101	13/07/2005	6	old	1	0.00	0.00	0.93	0.00	0.00	3.70	1.39
102	13/07/2005	7	new	2	0.00	0.00	0.47	0.00	0.00	1.40	3.27
103	13/07/2005	8	new	2	0.00	0.00	5.33	0.00	0.00	1.33	1.33
104	13/07/2005	9	new	2	0.00	1.82	0.00	0.00	0.00	1.36	0.91
105	13/07/2005	10	old	2	0.00	0.00	2.46	0.00	0.00	1.97	0.99
106	13/07/2005	12	old	2	0.00	0.00	1.89	0.00	0.00	3.30	2.36
107	13/07/2005	13	new	3	0.00	0.00	0.00	0.00	0.00	2.70	2.70
108	13/07/2005	14	new	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	13/07/2005	15	new	3	0.00	0.00	0.00	0.00	0.00	0.45	1.34
110	13/07/2005	16	old	3	0.00	0.00	1.38	0.00	0.00	1.84	1.38
111	13/07/2005	17	old	3	0.00	0.00	2.26	1.13	0.00	1.50	0.00
112	13/07/2005	18	old	3	0.00	0.00	0.77	0.00	0.00	0.77	0.00
113	23/08/2005	1	new	1	0.00	0.00	0.00	0.00	0.00	8.33	2.38
114	23/08/2005	2	new	1	0.00	0.00	5.00	0.00	0.00	15.00	0.00
115	23/08/2005	3	new	1	0.00	0.00	3.23	0.00	0.00	9.68	0.00
116	23/08/2005	4	old	1	0.00	0.00	0.43	0.00	0.00	3.04	2.61
117	23/08/2005	5	old	1	0.00	0.00	1.95	0.00	0.00	5.85	3.41
118	23/08/2005	6	old	1	0.00	0.00	2.23	0.00	0.00	4.02	2.23
119	23/08/2005	7	new	2	0.00	0.00	2.86	0.00	0.00	0.00	5.71
120	23/08/2005	8	old	2	0.00	0.00	0.00	0.00	0.00	3.39	3.81
121	23/08/2005	9	old	3	0.00	0.00	2.87	0.00	0.00	2.39	1.91
122	23/08/2005	10	old	3	0.00	0.00	1.46	0.00	0.00	1.46	0.00
123	07/09/2005	1	new	1	0.00	0.00	9.32	0.00	0.00	0.62	0.62
124	07/09/2005	2	new	1	0.00	0.00	2.94	0.00	0.00	0.98	1.96
125	07/09/2005	3	new	1	0.00	0.00	0.00	0.00	0.00	5.13	2.56
126	07/09/2005	4	old	1	0.00	0.00	0.00	0.00	0.00	3.25	1.18
127	07/09/2005	5	old	1	0.00	0.00	0.46	0.00	0.00	0.92	1.84
128	07/09/2005	6	old	1	0.00	0.00	0.42	0.00	0.00	6.25	2.50
129	07/09/2005	7	new	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	07/09/2005	8	new	2	0.00	0.00	0.00	0.00	0.00	10.00	0.00
131	07/09/2005	9	new	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	07/09/2005	10	old	2	0.00	0.00	1.00	0.00	0.00	0.50	0.50
133	07/09/2005	11	old	2	0.00	0.00	3.21	0.00	0.00	0.80	0.80
134	07/09/2005	12	old	2	0.00	0.00	1.59	0.00	0.00	3.59	1.99
135	07/09/2005	13	new	3	0.00	0.00	0.00	0.00	0.00	2.59	2.16
136	07/09/2005	14	new	3	0.00	0.00	0.00	0.00	0.00	1.50	4.00
137	07/09/2005	15	new	3	0.00	0.00	0.85	0.00	0.00	2.14	1.71
138	07/09/2005	16	old	3	0.00	0.00	0.00	0.98	0.00	3.41	0.98
139	07/09/2005	17	old	3	0.00	0.00	0.43	0.00	0.00	2.61	0.87
140	07/09/2005	18	old	3	0.00	0.00	2.26	0.00	0.00	3.62	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	AC134B	AC001B	AC022A	AC022C	AC013A	AC143A	AC048A	AC002A	AM001A	AU005E	AU005B
101	1.39	0.00	11.11	5.56	0.00	0.46	0.00	0.00	0.00	18.06	0.00
102	2.34	0.00	10.28	5.14	0.00	0.00	0.47	0.00	0.00	22.90	0.00
103	0.00	8.00	5.33	0.00	0.00	4.00	0.00	0.00	0.00	22.67	0.00
104	0.91	0.00	10.45	5.00	0.00	0.00	0.45	0.00	0.00	11.82	0.00
105	0.49	0.00	14.78	9.36	0.00	0.00	0.49	0.00	0.00	25.12	0.99
106	1.42	0.00	11.32	6.13	0.00	0.00	0.00	0.00	0.00	22.64	0.00
107	0.00	0.00	13.51	8.11	0.00	0.00	0.00	0.00	0.00	2.70	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	85.71	0.00
109	0.89	0.00	23.66	5.80	0.00	0.45	0.45	0.00	0.00	30.36	0.89
110	4.15	0.00	15.21	5.99	0.00	0.00	0.46	0.00	0.00	28.11	0.92
111	0.75	0.00	15.41	10.53	0.00	1.50	0.00	0.00	0.00	13.53	4.89
112	1.92	0.00	17.24	8.43	0.00	0.00	0.00	0.00	0.00	9.58	1.15
113	0.00	0.00	13.10	0.00	0.00	0.00	0.00	0.00	0.00	36.90	0.00
114	0.00	0.00	10.00	20.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00
115	6.45	0.00	9.68	16.13	0.00	0.00	0.00	0.00	0.00	45.16	0.00
116	0.43	0.00	11.74	10.00	0.00	0.43	0.00	0.00	0.00	17.83	0.87
117	2.93	0.00	9.27	10.73	0.00	0.00	0.00	0.00	0.00	19.51	0.00
118	1.34	0.00	9.82	16.07	1.34	0.00	0.00	0.00	0.00	9.82	0.00
119	0.00	0.00	20.00	2.86	0.00	0.00	0.00	0.00	0.00	14.29	0.00
120	0.42	0.00	13.98	13.98	0.42	0.00	0.00	0.00	0.00	13.98	2.54
121	0.48	0.00	9.09	3.83	0.00	0.00	0.00	0.00	0.00	11.00	0.00
122	0.00	0.00	6.83	3.90	0.00	0.98	0.00	0.00	0.00	4.39	0.49
123	0.00	0.00	11.80	3.73	0.00	0.00	0.62	0.00	0.00	18.01	0.00
124	0.49	0.00	7.84	10.78	0.00	0.00	0.00	0.00	0.00	42.16	0.00
125	0.00	0.00	7.69	5.13	0.00	0.00	0.00	0.00	0.00	10.26	0.00
126	0.59	0.00	8.28	7.99	0.00	0.00	0.59	0.00	0.00	13.61	0.00
127	0.46	0.00	12.90	9.68	0.00	0.00	0.00	0.00	0.00	39.63	0.00
128	1.25	0.00	7.08	7.92	0.00	0.00	0.00	0.00	0.00	22.08	0.83
129	0.00	0.00	20.00	6.67	0.00	0.00	0.00	0.00	0.00	20.00	0.00
130	0.00	0.00	5.00	5.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00
131	0.00	0.00	0.00	16.67	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	15.42	5.47	0.00	0.00	0.00	0.00	0.00	15.92	0.00
133	0.80	0.00	12.85	6.83	0.00	0.40	1.20	0.00	0.00	10.04	0.00
134	0.00	0.00	15.54	2.79	0.00	0.00	1.20	0.00	0.00	13.55	0.40
135	0.00	0.00	17.67	8.62	0.00	0.00	0.00	0.00	0.00	25.00	0.00
136	1.00	0.50	12.50	9.50	0.00	0.50	0.00	0.00	0.00	16.50	0.50
137	0.85	0.00	11.54	9.83	0.43	0.00	0.00	0.00	0.00	30.34	0.00
138	2.93	0.00	25.37	2.44	0.00	0.00	7.32	0.00	0.00	16.10	0.98
139	0.87	0.00	24.35	10.43	0.43	0.00	0.00	0.00	0.00	17.83	1.74
140	2.71	0.00	15.84	7.69	0.45	0.00	0.00	0.00	0.00	26.70	0.45

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	AU032A	AU9972	AU005A	AU004A	AU010A	AU010B	AU028A	BR006A	BR001A	BR003A	BR004A
101	0.00	2.31	0.46	0.00	0.00	0.00	0.93	1.85	0.00	0.00	0.00
102	0.00	0.93	1.40	0.00	0.00	0.00	0.00	1.87	0.00	0.00	0.00
103	1.33	0.00	0.00	0.00	0.00	0.00	0.00	1.33	0.00	0.00	0.00
104	0.45	0.91	0.00	0.00	0.00	0.00	0.00	5.45	0.45	0.00	0.00
105	1.48	0.49	0.00	0.00	0.00	0.00	1.48	1.97	0.00	0.00	0.00
106	0.47	0.00	0.00	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	5.41	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.46	2.30	4.61	0.00	0.00	0.00	0.92	0.46	0.00	0.00	0.00
111	1.13	1.88	0.00	0.00	0.00	0.00	1.50	0.00	0.00	0.00	0.00
112	0.00	0.38	0.00	0.00	0.00	0.00	1.15	0.77	0.00	0.00	0.00
113	9.52	1.19	0.00	0.00	0.00	0.00	0.00	2.38	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	1.74	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117	0.49	0.49	0.00	0.00	0.00	0.00	0.00	0.98	0.00	0.00	0.00
118	0.45	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
119	5.71	0.00	0.00	0.00	0.00	0.00	0.00	5.71	0.00	0.00	0.00
120	5.51	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00
121	0.96	0.48	0.00	0.00	0.00	0.00	0.00	9.57	0.00	0.00	0.00
122	1.46	0.00	0.00	0.00	0.00	0.00	0.00	6.83	0.00	0.00	0.00
123	1.24	1.24	0.00	0.62	0.00	0.00	0.00	0.62	0.00	0.00	0.00
124	3.92	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.56	0.00	0.00
126	0.30	0.30	0.00	0.00	0.00	0.00	1.18	0.30	0.00	0.00	0.00
127	2.30	0.46	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
128	1.25	1.25	0.00	0.00	0.00	0.00	1.67	0.00	0.42	0.00	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	1.49	0.00	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00
133	0.80	0.00	0.00	0.00	0.00	0.00	0.00	5.22	0.00	0.00	0.00
134	0.80	1.59	0.80	0.00	0.00	0.00	0.40	5.98	0.00	0.00	0.00
135	3.45	1.29	0.00	0.00	0.00	0.00	0.00	0.86	0.00	0.00	0.00
136	1.00	0.50	0.00	0.50	0.00	0.00	1.50	2.00	0.00	0.00	0.00
137	1.28	0.00	0.00	0.00	0.00	0.00	0.00	5.13	0.00	0.00	0.00
138	1.95	1.46	0.00	0.00	0.00	0.00	0.49	0.00	0.49	0.00	0.00
139	0.43	0.00	0.00	0.00	8.70	0.00	0.00	0.87	0.43	0.00	0.00
140	1.81	0.00	0.00	0.00	1.81	0.00	0.00	0.00	0.00	0.45	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	CO001A	CM008B	ENC01A	DT021A	DT004A	DP067A	CM046A	CM048A	EY017A	EY003A	EY010A
101	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.33
104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.91	0.00	0.00
105	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
106	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	2.70	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00
111	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
121	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
122	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
123	0.00	0.00	0.00	1.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
126	0.00	0.00	0.00	0.30	0.00	0.00	0.30	0.00	0.00	0.00	0.00
127	0.00	0.00	0.00	0.00	0.00	0.00	0.92	0.00	0.00	0.00	0.00
128	0.00	0.00	0.00	0.83	0.00	0.42	0.00	0.00	0.00	0.42	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.43	0.00
136	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
137	0.00	0.00	0.00	0.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
139	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.00	0.00	0.00	0.90	0.00	0.00	0.45	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EY011A	EY999A	EY016A	EY014A	EU047A	EU105A	EU015A	EU049B	EU070A	EU016A	EU009A
101	0.00	0.00	0.00	0.00	8.33	12.04	0.00	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	6.07	2.80	1.40	1.40	0.00	0.00	0.47
103	0.00	0.00	0.00	0.00	14.67	5.33	8.00	0.00	0.00	0.00	1.33
104	0.00	0.00	0.00	0.00	8.64	1.36	1.82	0.91	0.00	0.00	0.00
105	0.00	0.00	0.00	0.00	6.40	0.49	0.49	0.00	0.00	0.00	0.00
106	0.00	0.00	0.94	0.47	6.13	0.47	1.42	0.47	0.47	0.00	0.00
107	0.00	0.00	2.70	0.00	5.41	0.00	0.00	8.11	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	2.86	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	4.91	5.80	0.45	0.00	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	5.99	1.38	4.15	0.00	0.00	0.00	0.46
111	0.00	0.00	0.00	0.00	1.13	2.26	0.38	0.00	0.00	0.00	0.38
112	0.00	0.00	0.00	0.38	8.81	3.83	1.53	1.53	0.00	0.00	0.38
113	0.00	0.00	0.00	1.19	1.19	2.38	2.38	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	10.00	10.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	5.22	9.13	1.30	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	3.90	20.00	1.95	1.95	0.00	0.00	0.49
118	0.00	0.00	0.00	1.79	6.70	11.16	2.68	0.45	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	5.71	14.29	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	6.78	8.05	1.69	0.42	0.00	0.00	0.00
121	0.00	0.00	0.00	0.48	12.92	3.35	3.35	0.00	0.00	0.00	0.00
122	0.00	0.00	0.00	0.00	8.78	0.98	7.32	1.46	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	19.25	0.00	4.97	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00	5.88	1.96	3.43	0.00	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	2.56	7.69	5.13	0.00	0.00	0.00	0.00
126	0.30	0.00	0.00	0.00	5.03	2.37	0.89	0.00	0.00	0.00	0.00
127	0.00	0.00	0.00	0.00	3.23	1.84	2.30	0.00	0.00	0.00	0.00
128	0.00	0.00	0.00	0.00	3.75	0.83	0.00	0.00	0.00	0.00	0.42
129	0.00	0.00	0.00	0.00	6.67	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	10.00	0.00	5.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	33.33	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	1.00	0.50	15.42	1.99	3.98	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.00	10.04	1.20	2.41	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00	10.76	0.80	0.80	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.86	6.90	1.72	0.00	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	14.50	5.00	2.00	0.00	0.00	0.50	4.50
137	0.00	0.00	0.00	0.00	5.98	0.85	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	11.22	1.46	0.49	0.00	0.00	0.49	0.00
139	0.00	0.00	0.00	0.43	3.48	1.30	0.00	0.00	0.00	0.00	0.00
140	0.00	0.00	0.00	0.45	7.69	1.81	1.36	0.45	0.00	0.00	1.36

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EU010A	EU108A	EU035A	EU110A	EU040A	EU002A	EU002D	EU060A	EU003A	EU003B	EU003F
101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
103	0.00	0.00	1.33	0.00	0.00	0.00	2.67	0.00	0.00	0.00	0.00
104	0.00	0.00	0.91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
105	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
106	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	2.23	0.00	0.45	0.00	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.46	0.00	0.00
111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	0.00	1.19	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	6.45	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.85	0.00	0.00	0.00	0.00	0.00
121	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00
122	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	0.00	0.00	0.62	1.24	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00	0.00	0.98	0.00	0.00	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
126	0.00	0.00	0.00	0.00	0.00	0.30	0.00	0.59	0.00	0.00	0.00
127	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00
128	0.00	0.00	0.42	0.00	0.00	0.00	0.42	0.00	0.00	0.00	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00	0.86	0.00	0.43	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
137	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	0.00	0.49	0.49	0.00	0.00	0.00	0.00
139	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.00	0.00	1.36	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	EU003G	EU046C	EU008D	EU008A	EU039A	EU998A	EU045A	EU011A	FR006A	FR002A	FR002B
101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00
105	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
106	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.23	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00	0.00
121	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.35	0.00	0.00	0.00
122	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.46	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.96	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
126	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.59	0.00	0.00	0.00
127	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
128	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
137	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
139	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	FR009A	FR064Z	FR045A	FR005Z	FR007A	FU002B	FU002F	GO006A	GO020A	GO003A	NA037A
101	0.00	0.00	0.00	0.93	0.00	1.39	1.39	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.00	0.93	6.54	0.00	0.00	0.00	0.00
103	0.00	0.00	0.00	0.00	0.00	1.33	2.67	0.00	0.00	0.00	0.00
104	0.00	0.00	0.00	0.91	0.00	1.36	0.91	0.00	0.00	0.00	0.00
105	0.00	0.00	0.00	0.00	0.00	2.46	0.49	0.00	0.00	0.00	0.00
106	0.00	0.47	0.00	1.89	0.00	0.47	1.42	0.00	0.00	0.00	0.00
107	0.00	0.00	0.00	13.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	2.23	0.00	1.34	0.00	0.00	0.00	0.00	0.45
110	0.00	0.00	0.00	2.30	0.00	0.00	0.46	0.00	0.00	0.00	0.00
111	0.00	0.38	0.00	6.77	0.00	1.50	0.75	0.00	0.00	0.00	0.00
112	0.00	0.77	0.00	9.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	0.00	2.38	0.00	0.00	0.00	1.19
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	5.65	0.00	0.43	0.00	0.00	0.00	0.00	0.00
117	0.00	0.49	0.00	0.00	0.00	0.49	1.95	0.00	0.00	0.00	0.00
118	0.00	0.45	0.00	2.68	0.00	0.45	0.00	0.00	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	2.54	0.00	0.00	1.69	0.00	0.42	0.00	0.00	0.00	0.00	0.00
121	0.00	0.00	0.00	0.48	0.00	2.87	3.35	0.00	0.00	0.00	0.00
122	0.00	0.00	0.00	0.98	0.00	4.88	7.80	0.49	0.00	0.00	0.00
123	0.62	0.00	0.00	0.62	0.00	0.62	0.00	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.49	0.00	0.98	0.98	0.00	0.00	0.00	0.00
125	12.82	0.00	0.00	0.00	0.00	0.00	10.26	0.00	0.00	0.00	0.00
126	18.05	0.00	0.00	1.78	0.00	1.18	0.00	0.00	0.00	0.00	0.00
127	0.92	0.00	0.00	0.00	0.00	1.38	0.92	0.00	0.00	0.00	0.00
128	10.83	0.00	0.00	2.08	0.00	1.25	0.83	0.00	0.00	0.00	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	0.00	0.00	0.00	1.49	1.49	0.00	0.00	0.00	0.00
133	0.80	2.81	0.00	2.81	0.00	2.01	1.20	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	5.58	0.00	1.99	2.39	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	3.45	0.00	0.00	0.86	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	0.00	1.50	1.50	0.50	0.00	0.00	0.00
137	0.00	0.00	0.43	6.41	0.00	1.28	0.85	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.98	0.00	0.98	1.95	0.00	0.00	0.00	0.00
139	0.00	0.00	0.00	4.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.90	0.00	0.00	2.26	0.00	0.45	0.00	0.00	0.45	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NA045A	NA066A	NA751A	NA007A	NA046A	NA044A	NA003A	NA003B	NA068A	NA016A	NA006A
101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45
105	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
106	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.45	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46
111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38
113	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.42
121	0.00	0.00	0.00	0.00	0.00	0.48	0.00	0.00	0.00	0.00	0.48
122	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
124	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
126	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30
127	0.00	0.46	0.00	0.00	0.00	0.46	0.00	0.00	0.00	0.00	0.00
128	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.42	0.00	0.00	0.42
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	16.67	0.00
132	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.80
134	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40
135	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	0.00	0.00	0.00
137	0.43	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49
139	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NA013A	NA090A	NA650A	NA134A	NA033A	NA160A	NE006A	NE003A	NE003C	NE003B	NE036A
101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00	0.00	0.93
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45
105	0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00	0.00	0.00	0.00
106	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
111	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
121	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.44	0.00
122	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
126	0.00	0.00	0.00	0.00	0.00	0.30	0.00	0.00	0.00	0.00	0.30
127	0.00	0.00	0.00	0.46	0.00	0.46	0.00	0.00	0.00	0.00	0.00
128	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40
135	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
137	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
139	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.00
140	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	NE004A	NE020A	NI202A	NI027A	NI009A	PE002A	PI015A	PI015E	PI015C	PI015D	PI018D
101	0.93	0.00	0.46	0.00	1.85	0.93	0.00	0.00	0.00	0.00	0.00
102	0.00	0.00	0.00	0.00	0.93	1.40	0.00	0.00	0.00	0.00	0.47
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
104	0.00	0.00	0.00	0.00	0.00	5.45	0.00	0.00	0.00	0.00	0.00
105	0.00	0.00	0.00	0.00	0.00	4.43	0.00	0.00	0.49	0.00	0.49
106	0.00	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.00	0.00	0.00
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	0.00	1.79	0.00	0.00	0.00	0.00	0.89
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
111	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	1.19	0.00	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	1.30	0.00	0.00	0.00	0.00	0.43
117	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.89	0.00	0.45
119	0.00	0.00	0.00	0.00	0.00	2.86	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
121	0.00	0.00	0.00	0.00	0.00	4.78	0.00	0.00	0.00	0.00	0.00
122	0.00	0.00	0.00	0.00	0.00	8.29	0.00	0.00	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.62
124	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.56
126	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.30
127	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46
128	0.00	0.00	0.00	0.00	0.00	2.50	0.00	0.00	0.00	0.00	0.42
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.50	0.00	0.00	0.00	5.47	0.00	0.00	0.00	0.00	0.50
133	0.00	0.00	0.00	0.00	0.00	2.41	0.00	0.00	0.00	0.00	0.40
134	0.00	0.00	0.00	0.00	0.00	2.39	0.00	0.00	0.00	0.00	0.40
135	0.00	0.00	0.00	0.00	0.00	3.02	0.00	0.00	0.00	0.00	0.00
136	0.00	0.00	0.00	0.00	0.00	5.50	0.00	0.00	0.00	0.00	1.00
137	0.00	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.43	0.00	0.00
138	0.49	0.00	0.00	0.00	0.00	2.44	0.00	0.00	0.00	0.00	2.44
139	0.00	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.00	1.30
140	0.00	0.00	0.00	0.00	0.00	2.26	0.00	0.00	0.00	0.00	0.45

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	PI016A	PI008A	PI001A	PI005A	PI011A	PI022A	PI164A	PI997	PI007A	SR001A	SS002A
101	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.94
102	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	7.94
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
104	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.09
105	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
106	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.94	0.00	9.43
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
109	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00
110	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
111	0.00	0.38	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
112	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
113	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
114	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
116	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
117	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
118	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.23
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
121	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
122	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
123	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
124	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
125	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
126	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
127	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.46
128	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
129	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
132	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
133	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
134	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
135	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.72
136	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
137	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
138	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
139	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Appendix 4 Diatom species % relative abundance for Lochnagar epilithon, sampled 2004-2005. Diatom species codes are explained in Appendix 3.

no.	SA001A	SA012A	SP005A	SP006A	SU005As	SU005Ab	SU001A	SU030A	TA001Z	TA004A	TA003A	UNK	CC
101	0.00	0.00	0.00	0.93	0.00	0.46	0.00	0.00	12.04	0.00	0.00	0.93	6.48
102	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.68	0.00	1.87	2.80	5.14
103	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.67	0.00	0.00	0.00	14.67
104	0.00	0.00	0.00	0.00	2.27	0.00	0.00	0.91	15.91	0.00	0.00	0.00	5.91
105	0.00	0.00	0.00	0.00	1.97	0.49	0.00	0.00	16.26	0.99	0.00	0.00	10.84
106	0.00	0.00	0.00	0.00	0.47	1.89	0.00	0.94	12.74	0.47	0.00	0.00	8.02
107	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.41	0.00	0.00	0.00	2.70
108	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	11.43	0.00	0.00	0.00	5.71
109	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	6.70	0.00	0.00	0.00	12.05
110	0.00	0.00	0.00	0.00	0.00	0.46	0.00	0.00	6.45	0.00	0.00	0.00	8.29
111	0.00	0.00	0.00	0.00	0.75	0.00	0.00	1.13	9.02	0.00	0.00	0.75	5.64
112	0.00	0.00	0.00	0.00	0.00	0.38	0.00	0.00	9.20	0.00	0.00	0.00	4.21
113	0.00	0.00	0.00	0.00	1.19	0.00	0.00	0.00	8.33	0.00	0.00	0.00	5.95
114	0.00	0.00	0.00	0.00	0.00	5.00	0.00	0.00	10.00	0.00	0.00	0.00	15.00
115	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	9.68
116	0.00	0.00	0.43	0.00	0.43	0.00	0.00	0.00	12.17	0.00	0.00	0.00	4.35
117	0.98	0.00	0.00	0.00	0.98	1.46	0.00	0.00	6.34	0.00	0.00	0.98	11.71
118	0.00	0.00	0.00	0.00	0.89	0.45	0.00	0.00	11.61	0.00	0.00	0.00	7.59
119	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	20.00	0.00	0.00	0.00	14.29
120	0.00	0.00	0.00	0.00	0.42	1.27	0.00	0.00	7.63	0.00	0.00	0.85	5.93
121	0.00	0.00	0.00	0.48	0.48	0.00	0.00	0.00	16.75	0.00	0.00	0.00	10.05
122	0.00	0.00	0.00	0.00	1.46	1.46	0.00	0.00	18.54	0.00	2.93	0.00	3.41
123	0.00	0.00	0.00	0.00	1.24	0.00	0.00	0.00	9.32	0.00	3.11	1.24	3.73
124	0.00	0.00	0.00	0.00	0.49	0.00	0.00	0.00	6.37	0.00	0.49	0.00	7.84
125	0.00	0.00	0.00	0.00	5.13	0.00	0.00	0.00	5.13	0.00	0.00	0.00	15.38
126	0.59	0.00	0.00	0.30	0.30	0.00	0.00	0.00	4.44	0.30	0.59	0.00	13.02
127	0.00	0.00	0.00	0.00	0.46	0.46	0.00	0.00	2.76	0.46	0.00	0.00	17.51
128	0.00	0.00	0.00	0.00	1.25	0.00	0.00	0.00	2.08	0.00	0.00	1.67	21.25
129	0.00	0.00	0.00	0.00	13.33	0.00	0.00	0.00	26.67	0.00	0.00	6.67	26.67
130	0.00	0.00	0.00	0.00	10.00	0.00	0.00	0.00	25.00	10.00	0.00	0.00	30.00
131	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	33.33	0.00
132	0.00	0.00	0.00	0.00	0.00	0.50	0.00	0.00	22.89	2.99	0.00	0.00	9.45
133	0.00	0.00	0.00	0.00	0.80	0.40	0.80	0.00	10.44	0.40	0.00	1.61	10.04
134	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	6.37	1.59	0.00	3.98	12.75
135	0.00	0.00	0.00	0.00	1.72	1.29	0.00	0.43	6.90	0.00	0.00	0.43	15.09
136	0.00	0.00	0.00	0.00	1.00	1.50	0.00	0.00	4.00	1.00	0.50	0.00	15.50
137	0.00	0.00	0.85	0.00	0.00	0.00	0.00	0.00	2.99	0.00	0.00	0.00	9.40
138	0.00	0.00	0.00	0.00	0.49	0.49	0.00	0.00	6.34	0.00	0.00	0.00	8.78
139	0.00	0.00	0.00	0.00	0.87	0.00	0.00	0.00	7.83	0.43	0.00	0.00	11.74
140	0.00	0.00	0.45	0.00	0.90	0.00	0.00	0.00	4.52	0.00	0.00	0.00	23.53

Appendix 5 Oxygen isotope ratios of diatom silica for organic matter removal experiment. Replicate types: w = within run duplicates, b = between run duplicates.

Sample #	Treatment	Replicate type	Yield %	Raw $\delta^{18}O$ VSMOW	Run Correction ‰	Corrected $\delta^{18}O$ VSMOW	Mean within run	1σ within run	Mean between runs	1σ between runs
1	None	w	77.5	+27.08	-0.91	26.2	26.3	0.4	26.4	0.2
1	None	w	76.1	+27.31	-0.91	26.4				
1	None	b	74.3	+27.84	-0.84	27.0				
1	None	w	64.7	+27.32	-0.91	26.4	26.5	0.2		
1	None	w	68.9	+27.58	-0.91	26.7				
2	Ignition 550 AIR		76.3	+27.43	-0.91	26.5				
3	Ignition 550 AIR		75.4	+27.41	-0.91	26.5				
4	Ignition 550 AIR		77.1	+27.25	-0.91	26.3				
5	Ignition 950 AIR	w	78.9	+22.40	-0.91	21.5	21.7	0.3		
5	Ignition 950 AIR	w	77.2	+22.80	-0.84	22.0				
6	Ignition 950 AIR		80.7	+22.46	-0.91	21.6				
7	Ignition 950 AIR		77.9	+23.18	-0.29	22.9				
8	Ignition 450 VAC 4mB		68.8	28.15	-0.29	27.9				
9	Ignition 450 VAC 4mB	w	70.1	+27.69	-0.29	27.4	27.7	0.396		
9	Ignition 450 VAC 4mB	w	73.7	+28.25	-0.29	28.0				
9	Ignition 450 VAC 4mB	b	75.7	+27.88	-0.84	27.0			27.4	0.5
10	Ignition 450 VAC 4mB		68.9	+27.25	-0.29	27.0				
11	Ignition 250 VAC 4mB		70.4	+27.81	-0.29	27.5				
12	Ignition 250 VAC 4mB		66.1	+28.09	-0.29	27.8				
13	Ignition 250 VAC 4mB		66.4	+27.34	-0.86	26.5				
14	H2O2 30 hours	b	72.9	26.00	-0.34	25.7			25.8	0.2
14	H2O2 30 hours	b	70.6	27.56	-1.62	25.9				
15	H2O2 30 hours		75.7	26.93	-0.34	26.6				
16	H2O2 30 hours		72.4	27.22	-0.34	26.9				
17	H2O2 30 hours + HCL 2 hours	w	70.4	26.74	-0.34	26.4	26.6	0.3		
17	H2O2 30 hours + HCL 2 hours	w	71.4	27.11	-0.34	26.8				
18	H2O2 30 hours + HCL 2 hours		72.5	27.15	-0.34	26.8				
19	H2O2 30 hours + HCL 2 hours		73.9	27.53	-0.34	27.2				
20	H2O2 60 hours		71.5	+28.07	-0.86	27.2				
21	H2O2 60 hours		72	+27.71	-0.86	26.9				
22	H2O2 60 hours	b	71.7	+27.36	-0.86	26.5			26.6	0.1
22	H2O2 60 hours	b	77	+27.52	-0.84	26.7				
23	HNO3 30 hours		70.7	+28.50	-0.86	27.6				
24	HNO3 30 hours		82.4	+27.40	-0.99	26.4				
25	HNO3 30 hours		81.1	+27.82	-0.99	26.8				
26	HNO3 60 hours		81.2	27.66	-0.99	26.7				
27	HNO3 60 hours		80.3	27.70	-0.99	26.7				
28	HNO3 60 hours	w	81	27.63	-0.99	26.6	26.4	0.4		
28	HNO3 60 hours	w	80.1	27.05	-0.99	26.1				
29	Microwave		80.7	27.29	-0.99	26.3				
30	Microwave		82.2	27.29	-0.99	26.3				
31	Microwave		80.7	27.86	-0.99	26.9				
BFC (internal standard)		run A	81	29.43			29.64	0.35	29.75	0.151242
BFC (internal standard)		run A	79.7	30.00						
BFC (internal standard)		run A	80.8	29.79						
BFC (internal standard)		run A	79	28.89						
BFC (internal standard)		run A	78.1	29.45						
BFC (internal standard)		run A	78.7	29.62						
BFC (internal standard)		run A	75.4	29.85						
BFC (internal standard)		run A	81.2	29.74						
BFC (internal standard)		run A	82.7	30.00						
BFC (internal standard)		run B	78.8	28.98			29.86	0.773		
BFC (internal standard)		run B	79.5	29.45						
BFC (internal standard)		run B	74.0	30.35						
BFC (internal standard)		run B	77.4	30.64						

Appendix 6 Oxygen isotope ratios of diatom silica collected from Lochnagar using artificial substrata. (a) Samples with no spiking; (b) Samples spiked with quartz silica. Replicate types: w = within run, b = between run.

(a)

Sample #	Sample date	Replicate type	Yield %	Raw $\delta^{18}O$ VSMOW	Run Correction ‰	Corrected $\delta^{18}O$ VSMOW	Mean within run	1σ within run	Mean between runs	1σ between runs
1	05/05/2004		61.4	+33.01	-1.86	31.2	31.0	0.2		
1		w	62.0	+32.27	-1.35	30.9				
2	02/06/2004		67.5	+33.26	-1.86	31.4				
3	25/08/2004		74.4	+32.25	-1.35	30.9				
3		b	75.1	+32.40	-1.35	31.1			31.0	0.1
4	22/09/2004		72.3	+30.72	-1.35	29.4				
5	17/11/2004		71.7	+32.73	-1.35	31.4				
6	23/03/2005		62.2	+35.49	-1.35	34.1				
6		w	56.2	+34.49	-0.7	33.8	34.0	0.2		

(b)

Sample #	Sample date	Diatom mg	Quartz mg	Total yeild %	Est. diatom yeild	Est. diatom mg. (after pre-fluorination)	Total $\delta^{18}O$ VSMOW	Quartz $\delta^{18}O$ VSMOW	Est. diatom $\delta^{18}O$ VSMOW
7	30/06/2004	3.33	5.14	83.2	61.90	2.06	16.6	9.62	33.9
8	20/10/2004	3.88	2.64	76.5	62.55	2.43	21.1	9.62	33.5
9	20/04/2005	3.32	3.05	79.5	63.42	2.11	17.7	9.62	29.4
10	22/05/2005	2.69	3.88	79.1	53.28	1.43	15.2	9.62	30.3
11	23/08/2005	4.74	1.76	61.4	48.18	2.28	22.0	9.62	31.6
12	07/09/2005	2.06	4.24	81.7	50.21	1.03	14.8	9.62	35.8
13	08/10/2005	2.85	3.95	80	56.44	1.61	17.3	9.62	36.3

Appendix 7 Oxygen isotope ratios of diatom silica collected from lake surface sediments across Europe. Replicate types: w = within run, b = between run.

Sample #	Site Name	Replicate type	Yield %	Raw $\delta^{18}O$ VSMOW	Run Correction	Corrected $\delta^{18}O$ VSMOW	Mean within run	1σ within run	Mean between runs	1σ between runs
1	Syrjanalunen, FINLAND		74.5	+21.07	0.17	+21.24				
2	Oikojarvi, FINLAND		76.5	+22.29	0.17	+22.46				
3	Keltjoru, SWEDEN		78.7	+21.62	0.17	+21.79				
4	Tunturilampi, FINLAND		69.5	+23.03	0.32	+23.35	23.3	0.03		
4		w	69.8	+22.99	0.32	+23.31				
5	Hirviiankurunlampi, FINLAND		74.7	+22.03	0.32	+22.35				
6	Syrjanalunen, FINLAND		73.4	+24.64	0.32	+24.96				
7	Lago Grande di Monticchio, ITALY		73.0	+33.80	0.32	+34.12				
8	Lough Neagh, NORTHERN IRELAND		70.8	+32.19	-1.86	30.3			30.4	0.1
8		b	65.8	+32.36	-1.86	30.5				
9	Lac d'Aydat, FRANCE		69.3	+32.22	-1.86	30.4				
10	Lac de la Cousteix, FRANCE		71.9	+31.94	-1.86	30.1				
11	Kiuvajarvi, FINLAND		70.7	+28.64	-1.86	26.8				
12	Lac des Corbeaux, FRANCE		72.1	+31.86	-1.86	30.0				
BFC (internal standard)			79.1	28.58						
BFC (internal standard)			N/A	28.84						
BFC (internal standard)			76.0	28.87						
BFC (internal standard)			76.5	28.24						
BFC (internal standard)			72.0	29.25						
BFC (internal standard)		b	78.8	30.74						